Inkjet Printing of 3D Metallic Silver Complex Microstructures

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Abstract

To broaden the scope of inkjet printing, this paper focuses on printing of an organic silver complex ink on glass substrates towards the fabrication of metallic 3D microstructures. The droplet formation sequence of the inkjet printer is optimised to print continuous layers of metal. A brief discussion on orientation trials, aimed at optimising the print parameters, is followed by two different methodologies of printing 3D microstructures: wet-in-wet and wet-in-dry. The surface topography of the end product and the possibility to stack layer-upon-layer using these two methodologies are the main criteria investigated in this paper.

Keywords

Inkjet Printing, Microfabrication, Rapid Prototyping & Manufacturing, Nanoparticles

1 INTRODUCTION

Inkjet printing is an additive process that can potentially reduce material wastage, enhance flexibility and reduce the number of process steps. It can be classified under rapid manufacturing as well as maskless manufacturing techniques. In the context of electronics fabrication, inkjet printing has made rapid strides of late, and is seen as a key enabler to the widespread application of printed electronics or organic electronics. Most of the current research activities dealing with inkjet printed electronics involve printing of a single ink layer which, after curing, would either serve the intended purpose as such, or act as a seed layer for a subsequent plating process. Some examples for the former can be found in [1-3], while a recent example for inkjet printing of a seed layer for electroless plating was published in [4].

Development of inks with low sintering temperature, such as a nanoparticle-based silver ink, has given a major impetus to research activities in this field. These nanoparticle inks consist of metal nanoparticles, typically silver or gold, dispersed in a solvent that enables the ink to be jetted from the nozzle of an inkjet printer. Due to the so-called thermodynamic size effect [5], the melting point of nanoparticles drops drastically in comparison with that of the bulk metal. For instance, bulk gold melts at more than 1000°C, whereas nanoparticle gold with a diameter of 2 nm melts approximately at 150°C [6]. But in most cases, the nanoparticles are not heated till they melt; they are subjected to heating below their melting temperature, leading to a combination of particle growth and grain-boundary migration [7]. The reason is, typical nanoparticle inks available in the market for inkjet printing have a particle size of 5 nm to 10 nm, and the melting point of such particles is much higher than the value quoted above, making melting impractical for most applications. Ideally, the sintering process should vaporise all the solvent as well as additives present in the ink, so that the sintered metal is close to 100% dense. The recommended sintering temperatures of the nanoparticle-based inks currently available are in the order of 150°C - 200°C. There is another type of ink available in the market, based on a non-particle formulation containing an organic silver complex compound [8]. This ink type has a lower sintering temperature than most nanoparticle-based inks, making it suitable for a wider range of substrates. However, even in this case, the sintering temperature is generally more than 100°C.

This study aims to broaden the scope of inkjet printing to encompass application areas that are closely associated with electronics such as capillary microstructures for cooling of electronic circuits [9], as well as other application areas such as lab-on-a-chip and microelectromechanical systems (MEMS). Even though such applications of inkjet printing have already been discussed in [10] and [11], there are still some missing pieces to the jigsaw puzzle, namely the feasibility to stack inkjet printed layers (i.e. layer-upon-layer) to fabricate 3D microstructures and the challenges that need to be overcome to achieve the same. These bring in new factors such as surface roughness of the stacked layers, their cohesion, faults induced due to thermal stresses resulting from sintering, accuracy of multiple stacked layers etc. This paper focuses on different ways of printing 3D metallic microstructures, and the resulting issues namely surface roughness and accuracy of the end product.

2 EXPERIMENTAL PART

2.1 Materials and methods

An organic silver complex compound (TEC-IJ-040 from Inktec Co. Ltd., South Korea) was used as the functional ink to generate structures on glass substrates. According to the suppliers, the organic silver complex compound makes up less than 77% of the ink by weight; the rest is made up of methanol and anisole. To extract the silver component of the ink, it should be sintered at 150°C for 30 minutes. A commercially available drop-on-demand inkjet printer (Jetlab-4, from MicroFab Technologies Inc., USA) was used for all the printing trials. The printer is capable of independent X, Y and Z-stage movement, with the first two used to position the substrate holder, and the Z-stage, to adjust the height of the printhead on which the nozzle is mounted. All the layers were printed using a piezo-actuated nozzle with an inner diameter of 80 µm. It is possible to heat up the substrate holder and the printhead independently up to 100°C. The printer is equipped with two stroboscopic cameras, one to observe the droplet formation from the nozzle, and the other, mounted vertically with respect to the plane of printing, to view the results of printing on the substrate. Interferometric analyses of the printed structures were performed using a Micromap 560 (from ATOS GmbH, Germany), to determine their surface roughness and thickness. An optical microscope (Leitz DMRX from Leica Microsystems, Germany) was used for studying the edges/boundaries of the structures.

2.2 Orientation trials

Before inkjet printing layer-upon-layer, single dots and single layers of silver were printed and analysed. Figure 1 shows the droplet formation sequence from the nozzle of the inkjet printer. As seen from the sequence of pictures in this figure, a jet of the ink is formed due to piezo-actuation that gives rise to a pressure wave. The jet then breaks up creating a droplet. This is explained by the Rayleigh-Tomotika instability, according to which the jet breaks up if the wavelength of the disturbance i.e. pressure wave is greater than the diameter of the jet [12].

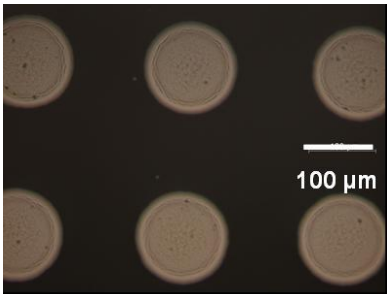


Figure 2 - Inkjet printed droplets after spreading on a glass surface.

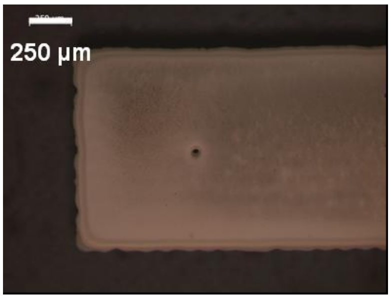


Figure 3 - A structure printed by depositing a rectangular array of droplets on a glass substrate.

Figure 2 shows a glass slide on which individual silver droplets were printed and Figure 3 shows a glass slide on which a continuous layer was printed. The extent of droplet spreading on the substrate depends on the surface tension of the ink and the surface energy of the substrate material. In general, if the surface energy of the substrate is high, the droplet spreading is more and the contact angle is small. Depending on the application, the surface properties of the substrate can be modified to make it hydrophilic or hydrophobic, and consequently influence droplet spreading. The droplet spacing was adjusted in X and Y directions (Z being the thickness direction) to obtain a continuous printed structure like the one shown in Figure 3. However, arbitrary values for X and Y pitch cannot be chosen; instead, they should be determined empirically to avoid cross-sectional irregularities. This is illustrated by Figure 4: a single line, i.e. a structure printed by adding droplets in only one direction, was printed with 3 different droplet spacing: 100 µm, 110 µm and 120 µm. The line printed with 100 µm spacing is the best one of the lot. Scalloping of the edges of the lines printed with the other two droplet spacing values could be observed from the figure. If the spacing is reduced below 100 µm, bulging of the line is observed.

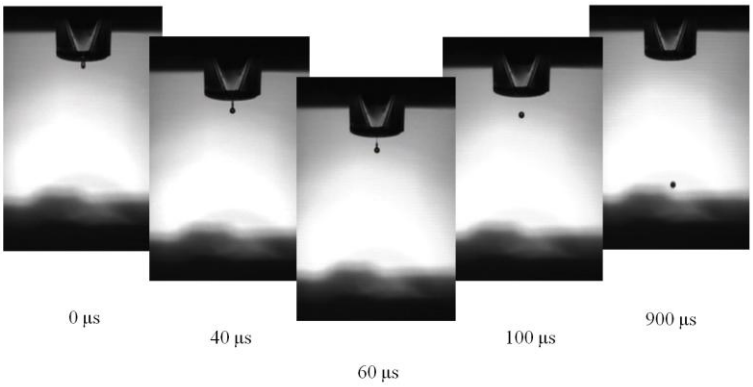


Figure 1 - Droplet formation from the nozzle of an inkjet printer.

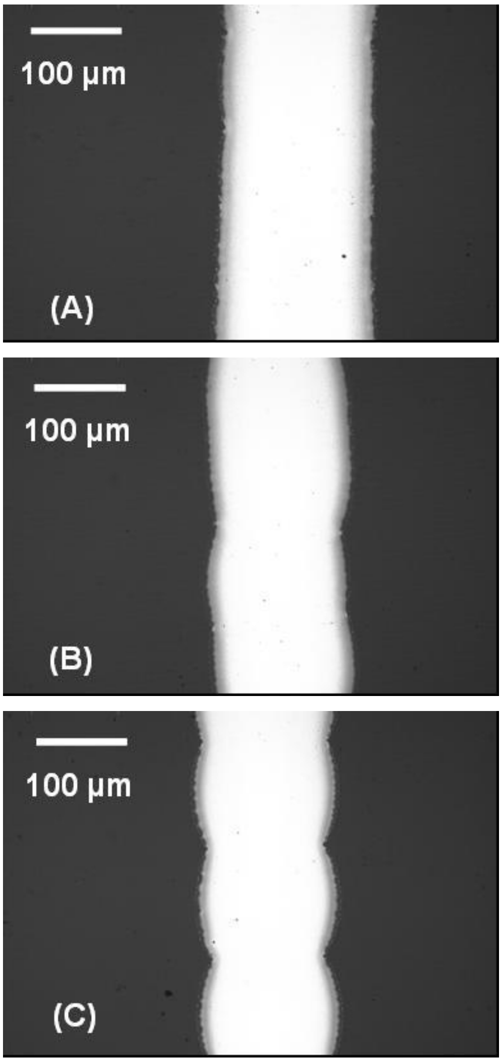


Figure 4 - Inkjet printed lines on a glass substrate with (A) 100 µm droplet spacing, (B) 110 µm droplet spacing and (C) 120 µm droplet spacing.

2.3 Printing of 3D microstructures

There are 2 possibilities to fabricate 3D microstructures using inkjet printing: (1) wet-in-wet and (2) wet-in-dry. Wet-in-wet printing involves printing a layer of ink without drying the previous layer i.e. the previous layer is still in a ‘wet’ condition. Wet-in-dry printing could be done in 2 ways: (a) printing a layer after the previous one is minimally heated to remove the solvent and other non-metallic content of the ink, or (b) printing a layer after the previous one is sintered completely. In this research, only the former approach along with wet-in-wet was followed. The approach where the previous track is completely sintered was impractical with the available setup, as the substrate has to be heated to 150°C for complete sintering. As already mentioned, the available substrate holder could be heated only up to 100°C. When the sintering was done externally, the lack of pick-and-place devices led to positional inaccuracies. Hence, from here on, wet-in-dry refers only to the chosen method of minimal heating of the substrate. In this case, the temperature of the substrate holder was maintained at 90°C to induce flash evaporation of the solvent and other non-metallic components. This gave rise to another problem: since the nozzle of the printer is very close to the substrate (1 mm), the flow properties of the ink were altered during printing as a result of an increase in temperature. The change in properties of the ink resulted in an increase in droplet size and frequent blocking of the nozzle due to solvent evaporation. Nevertheless, this approach was followed due to even more complex problems involved in external heating.

With a droplet pitch of 100 µm in X and Y directions, multiple layers were printed on glass substrates in wet-in-wet and wet-in-dry modes. In both cases, the subsequent layers were printed without any pause in between. The only difference between them is the influence of substrate heating. Initially, 3 stacked layers were printed in both cases and the printed structures were observed with an optical microscope and interferometer. Surface roughness and layer thickness of the structures were the criteria studied. Based on the results of the analyses, it was decided to continue only with the wet-in-dry approach. Up to 5 stacked layers were printed using this approach and analysed.

3 RESULTS AND DISCUSSION

The structures printed using the wet-in-wet approach highlighted the following shortcomings: (1) there was no linear or quasi-linear increase of thickness of the printed structure with the increase in number of layers, as shown in Figures 5(A) to (C), and (2) the surface roughness was pronounced and unsuitable for most practical applications on thrice-printed structure as can also be seen in Figure 5(C). It was also observed that the increase in line thickness in this case was less than the other (wet-in-dry) approach.

Figure 5 also clearly shows that a single layer has a curved profile (cross-section) whereas the subsequent layers led to the flattening and widening of the cross-section. This can be attributed to the impact of a droplet on the previous undried one and the subsequent re-arranging influenced by the surface tension of the ink as well as the surface energy of the substrate. Figure 6 shows the flattening of the undried first droplet when a second droplet is deposited on it.

The high surface roughness seen in Figure 5(C) can be attributed to the drying process; however, the exact mechanism is not clear. As mentioned, the surface roughness of the printed structure increased markedly after the second layer. It was also observed from the lines printed using the wet-in-wet approach that the line width increases with the number of layers. This can be clearly seen from Figures 7(A) to (C).

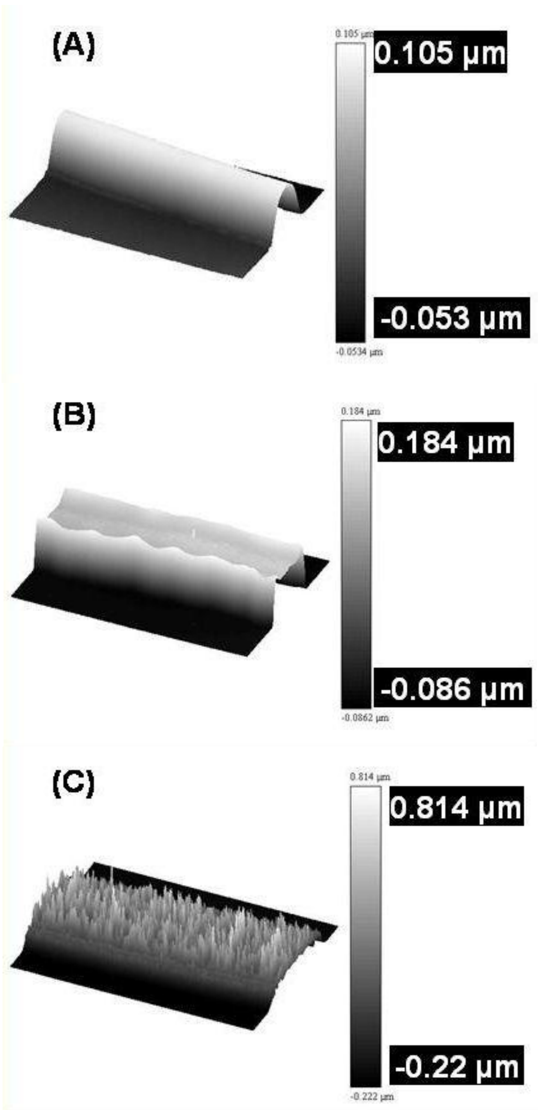


Figure 5 - 3D interferometric images of inkjet printed microstructures (wet-in-wet) on glass, containing (A) 1 layer, (B) 2 stacked layers, and (C) 3 stacked layers.

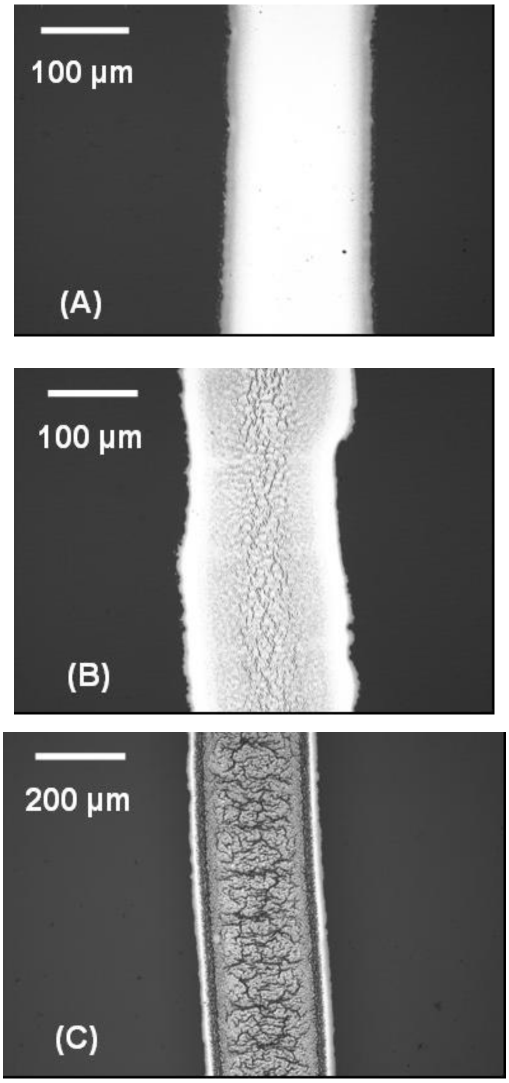
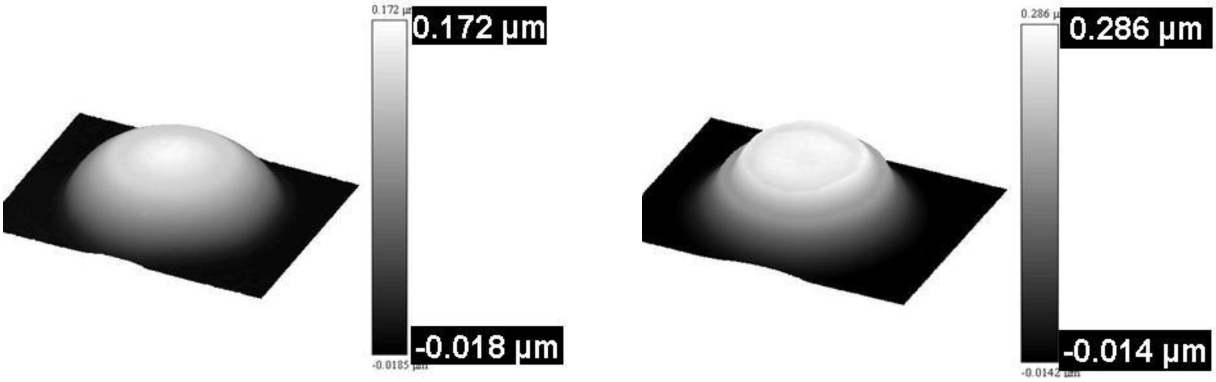


Figure 7 - Micrographs of inkjet printed microstructures (wet-in-wet) on glass, containing (A) 1 layer, (B) 2 stacked layers, and (C) 3 stacked layers. It can be clearly seen here that the structure shown in (C) has a very irregular surface topology.



(a) single droplet

(b) two droplets (wet-in-wet)

Figure 6 - 3D interferometric images of inkjet printed droplets on glass.

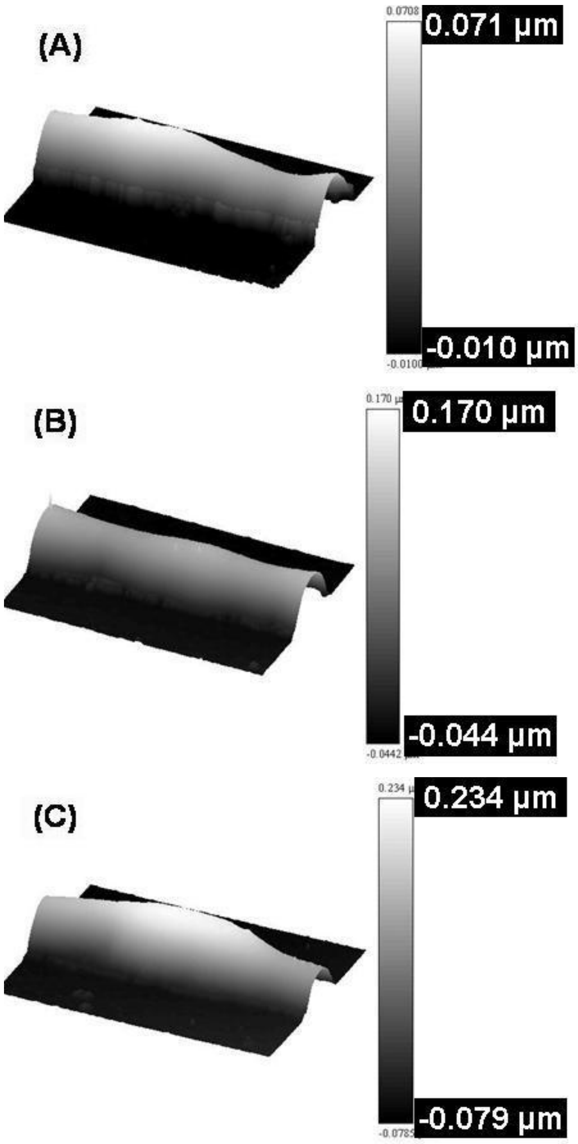


Figure 8 - 3D interferometric images of inkjet printed microstructures (wet-in-dry) on glass, containing (A) 1 layer, (B) 2 stacked layers, and (C) 3 stacked layers.

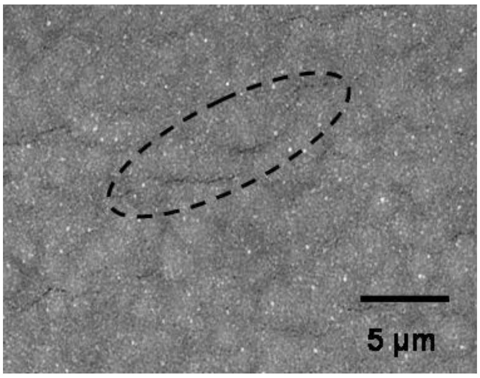


Figure 9 - Cracks on an inkjet printed layer after sintering.

The wet-in-dry approach yielded better results in terms of the increase of layer thickness with the number of layers – the increase was quasi-linear, as shown in Figures 8(A) to (C). Moreover, there was no marked change in layer width. This can be attributed to the relative rigidity of the printed layer due to the evaporation of the solvent. As a result of this, when the next layer was printed, the spreading of the ink is not as pronounced as in the previous case. Also, the printed structures were not as rough as those printed using the previous approach. These 3 criteria, viz. quasi-linear increase in layer thickness, minimal increase in line width and low surface roughness values were met satisfactory by the wet-in-dry approach for up to 5 stacked layers.

Irrespective of the method of printing, cracks were seen on printed layers after sintering. An example of this is shown in Figure 9. This can be attributed to the stresses induced due to sintering and subsequent cooling. These cracks have a detrimental effect on the integrity of inkjet printed 3D microstructures.

4 CONCLUSIONS AND RECOMMENDATIONS

The droplet spacing (pitch) is crucial for the build-up of 3D microstructures, in order to avoid bulging or scalloping of the printed structure. The wet-in-wet approach leads to much wider structures than intended and hence is not the right approach to print 3D microstructures. Moreover, it also results in higher surface roughness and lower thickness of printed structures than the corresponding wet-in-dry approach.

The wet-in-dry approach was found to be the suitable approach to inkjet printing of 3D microstructures. Further investigations are needed to ascertain the suitability of this approach to print much thicker structures that need stacking of 10 or more inkjet printed layers. This could eventually lead to the commercial application of this approach for microfabrication.

Though only one type of ink was used in this study, the methodology adopted can be applied to other types of inks as well. Moreover, in cases where the end product needs to be fabricated using metallic inks, inkjet printing can be used to print just the seed layer; subsequently, copper can be plated on this seed layer to achieve the desired layer thickness. This has certain advantages, as discussed in [4]. This paper was published under the same research framework as this study.

It is recommended to test the printed structures containing multiple stacked layers for adhesion and cohesion, to find out how robust the end products are. Peel test, pull-off test and scotch tape test are some of the testing methodologies that can be used for this purpose. It would also be worthwhile to find out ways to minimise the formation of cracks on printed structures after sintering.

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6 BIOGRAPHY

Wessel Wits received his Ph.D. and Master's degree in Mechanical Engineering from the University of Twente in Enschede, The Netherlands in 2008 and 2004, respectively. Currently, he is an assistant professor at the Laboratory of Design, Production and Management at the University of Twente. He is also a research affiliate of the International Academy for Production Engineering (CIRP).

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