A Combined Ink Jet Printing/Photo-reduction Process for the Fabrication of μm-size Conductive Tracks

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Abstract

Ink jet printing is a promising process for the production of cheap, flexible electronic circuits. Miniaturisation of such circuits to sizes smaller than currently attainable by conventional ink jet printing would present benefits in terms of performance, economics and the environment. Two laser-based techniques (selective laser ablation and photo-reduction) used in conjunction with ink jet printing to reduce feature size are demonstrated. Selective laser ablation of metallic silver tracks enabled feature sizes to be reduced to ~5 μm, with good edge definition and little damage to glass substrates. Photo-reduction of organometallic silver salt deposits enabled features down to ~10 μm, with no measurable heating of the substrate; enabling the use of a wide range of polymeric substrates. Both techniques show potential for reducing the feature size of ink jet printed deposits by an order of magnitude on flexible substrates.

Introduction

The drive for cheap, flexible electronics has resulted in a large amount of research into alternative techniques to traditional silicon device fabrication [1-3]. Ink jet printing is one such technique that has additional advantages such as simultaneous multi-material deposition and the lack of any masks. Ink jet printing produces components by ejecting a small (1-1000 pl) droplet of material-laden ink towards a pre-determined location on a substrate; this droplet will spread upon impact with the substrate and change phase to form a solid deposit.

The need for a liquid precursor, combined with the desire to use flexible polymer substrates, prevents the use of many conventional functional materials due to the need for low temperature processing. Functional polymers in solution have been successfully printed to fabricate transistors [3] and polymer-LED displays [4]. While readily printable and requiring only low temperature heat treatments, the electrical performance of functional polymers is inferior to traditional functional materials. In addition, functional polymers often have poor stability in ambient environment, particularly to oxygen and water [4]. Nanoparticle suspensions of more conventional functional materials have been successfully printed to fabricate MEMS devices [5] and conductive tracks [6], with the reduced particle size resulting in a significant reduction in melting temperature that enables low temperature processing [7]. Conductive tracks printed using a silver nanoparticle ink obtain a conductivity approaching that of bulk silver after heat treatments between 200-300 °C [6]. Organometallic silver salts in solution have also been printed, with conductivities approaching bulk silver achieved with heat treatments as low as 150 °C [8].

The size of features that can be manufactured by inkjet printing is limited by the size of droplet generated and how the droplet interacts with the substrate; typically this corresponds to ~50 μm. To achieve the size of component necessary for circuits of higher complexity, this size would have to be reduced to approaching μm-size and smaller. Any reduction in size also has the advantage of using less material in the manufacture of each component, which has economic and environmental benefits. Several methods have been investigated to try and reduce the size of ink jet printed features, including the use of surface energy patterning [3], fluid-assisted dewetting [9], and laser curing of nanoparticles [10].

The use of lithographic methods is widespread in the patterning of electronic components; however, only a limited number of such techniques are applicable to ink jet printing of electronic circuits due to the use of chemicals incompatible with polymeric materials [11]. Methods that avoid the use of such chemicals and that can be adapted to a continuous processing environment show the greatest potential for combining with ink jet printing for device fabrication.

UV laser ablation is one such technique that utilises short (~ 10^{-9} s), high energy laser pulses to selectively remove material from a surface. The energy from the laser pulse is absorbed by only by material at the surface of the target, which is instantaneously evaporated. The short timescale involved means that there is not enough time for any heat transfer to occur to the bulk of the target material, leaving all but the removed material unaffected by the process. This process has previously been used to remove thin films of gold from polymer films [11-12].

The photolysis of organometallic silver salt films has long been known about [13-14]. A reduction of the silver ion within the salt by charge transfer with the carboxylate group is initiated by irradiation with light. This forms photolytic colloidal silver particles within the salt that are seen as a brown hue to the salt film. Upon further irradiation with light of the appropriate wavelength, the film takes on a metallic appearance and eventually becomes mirror-like. Previous work has looked at irradiation of the salt with a relatively low intensity light source, which resulted in a thin metallic film only at the exposed surface of the deposit [14].

Experimental Procedure

Ink Jet Printing

The ink used in this study was an organometallic salt dissolved in xylene synthesised in-house, preparation details for which have been published previously [8]. Printing of samples was carried out using a JetLab printing platform (MicroFab Inc., Plano, TX, USA) that consists of a piezoelectric squeeze mode print head situated above a programmable x-y platform. The print heads used in this study had a nozzle diameter of 60 µm (MJ-AB-01-60, MicroFab, as above). All samples were printed onto glass substrates (microscope slides, BDH, Poole, Dorset, UK) that had been cleaned in acetone.

Selective Laser Ablation

Printed samples were heat treated at 180 °C for 30 minutes to convert the organometallic deposit into silver. Tracks were placed on an x-y platform and partially exposed to a pulsed KrF UV-excimer laser (λ=248 nm, FWHM=30 ns) previously shaped by inserting a square aperture into the beam path (Figure 1a). Fine features are achieved by selectively exposing only the areas of silver that should be removed.

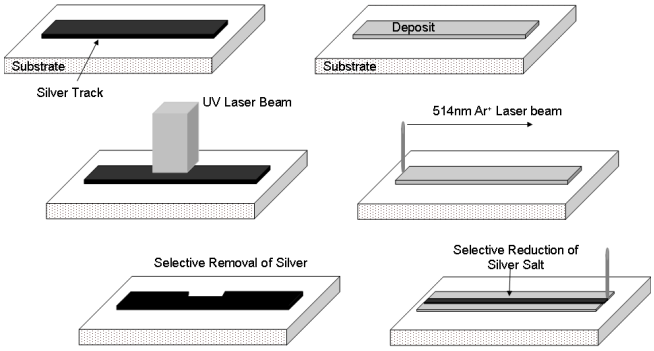

Figure 1 *Schematic representations of a) selective laser ablation and b) photo-reduction processes to produce µm-size conductive silver tracks*

Photo-reduction

The sensitivity of produced organometallic deposits to different wavelengths of light was measured using a UV-Vis spectrometer (ATI UNICAM, UV2) with data collected every 2 nm. A laser was targeted towards the printed deposit, with the laser spot moved relative to the substrate to obtain a linear deposit (Figure 1b). Initial work used a continuous Ar^+ ion laser (Spectra-Physics, model 2017, 200 mW power, λ=514.5 nm, spot size ~300 µm). To obtain finer features, a Renishaw Ramascope Raman spectrometer with a continuous Ar^+ ion laser (20mW power, λ=514.5 nm) was used. The laser spot size was reduced to ~10 µm by means of an Olympus BH2-UMA microscope fitted with a 20 times objective lens.

Dimensions of produced deposits were obtained using phase contrast microscopy (PCM) (MicroXAM, ADE Phase Shift, Tucson, AZ, USA).

Results and Discussion

Selective Laser Ablation

Figure 2 shows a silver track that has been selectively ablated to achieve a feature size of ~5 µm. The edge definition obtained with this method is good, with a sharp transition between silver deposit and substrate. Little damage was observed to the glass substrate, and further optimization of the number and intensity of ablative pulses would lead to similar results on flexible polymer substrates.

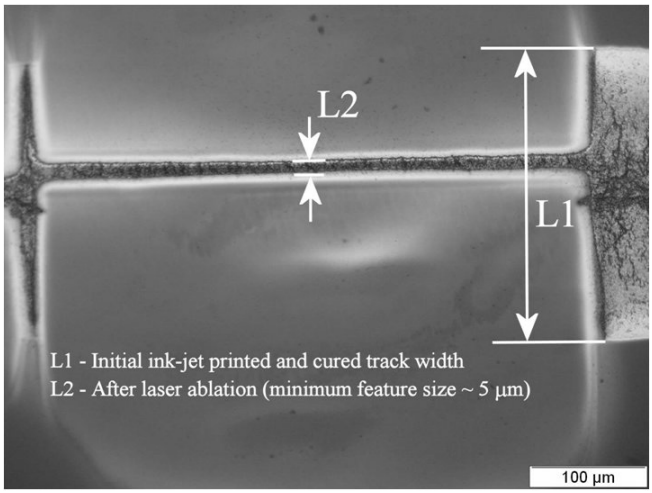

Figure 2 *A selectively ablated silver track, showing a feature size reduced to approximately 5 µm*

Photo-reduction

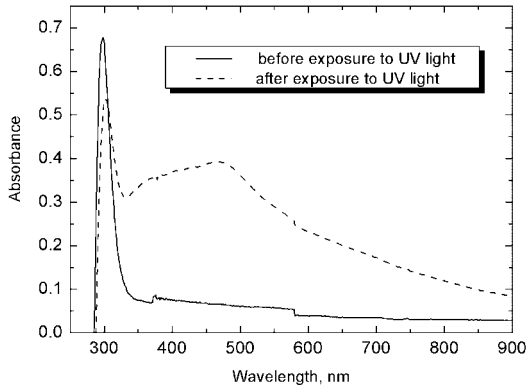

Figure 3 *UV-Vis spectra of organometallic silver salt deposits before and after exposure to UV light*

The UV-Vis spectra of the organometallic deposit was found to have a strong absorption of light at λ~300 nm (Figure 3),

corresponding to the photolytic reduction of the Ag^+ ion. After exposure to UV light a much broader peak was found at 350-550 nm, which corresponds to the absorption spectra of the photolytic colloidal silver particles present within the film.

Irradiation of organometallic deposits with a 300 μm spot size laser produced a highly reflective metallic deposit instantaneously (Figure 4). A thermocouple was placed on the rear of the glass slide to measure any increase in temperature during the reaction. No temperature increase was detected, indicating that any heat affected zone is localized around the laser spot. The good agreement between area of converted material and laser spot size also indicates a localization of any heating, indicating the suitability of photo-reduction to the use of temperature sensitive substrates.

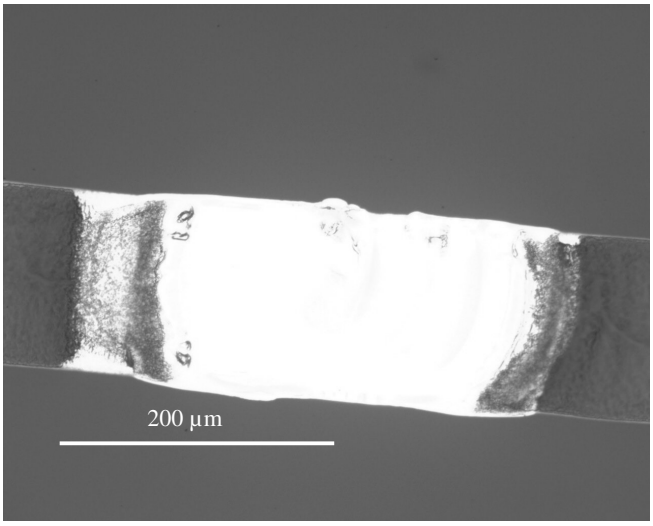

Figure 4 *A photo-reduced organometallic silver salt track*

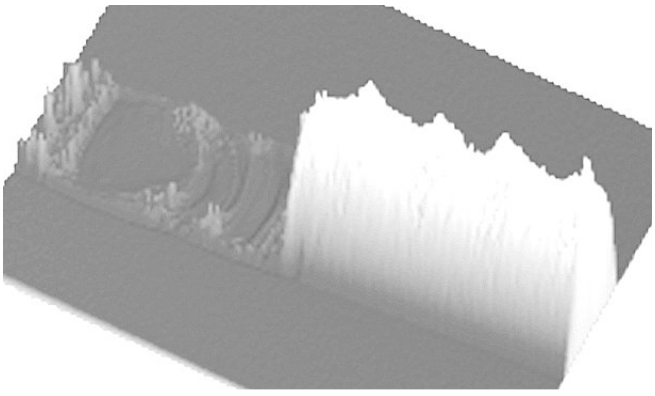

Figure 5 *PCM micrograph of photo-reduced organometallic silver salt track, showing 90+% reduction in deposition thickness upon photolysis*

PCM micrographs of obtained deposits showed a 90+% decrease in deposit thickness upon photolysis to 150-200 nm (Figure 5). This amount of reduction indicates that the full thickness of deposit was converted to metallic silver, rather than just the exposed surface conversion obtained with lower intensity light [14]. The thickness upon photolysis is appreciably smaller than that obtained upon a standard heat treatment, indicating that the speed of the reduction and decomposition may increase the packing density of produced silver grains.

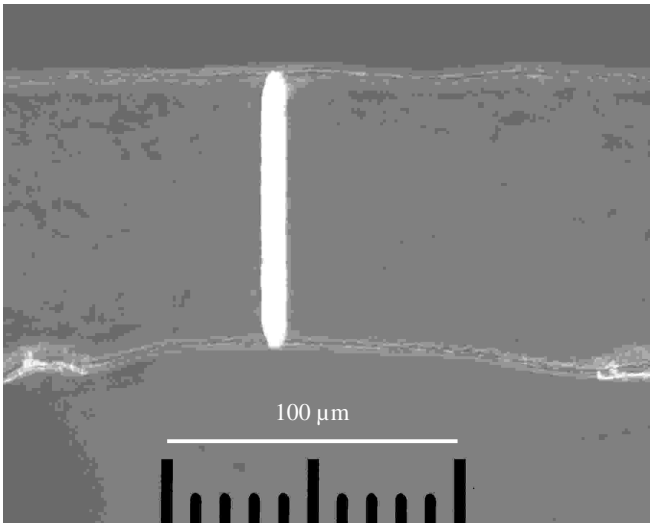

Figure 6 *An organometallic silver salt track photo-reduced by and Ar^+ laser of ~10 μm spot size.*

Samples irradiated with a smaller spot size Ar^+ laser were also found to instantaneously produce metallic silver deposits (Figure 6). Features of ~10 μm were obtained, corresponding to the spot size and indicating good edge definition for the reduced deposit.

Conclusion

Conductive track of μm-size dimensions is a necessity for the production of cheap, flexible electronic circuits. Two different methods of using lasers to reduce the feature size of ink jet printed deposits were demonstrated. Both selective laser ablation of silver tracks and photo-reduction of silver organometallic salt were able to decrease feature by an order of magnitude to less than 10 μm with good edge definition. Photo-reduction of deposits led to no bulk heating of the substrate, indicating the suitability of such a technique to temperature sensitive polymer substrates.

Acknowledgements

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Biography

Jonathan Stringer is currently in the final year of his PhD in the School of Materials at the University of Manchester, United Kingdom. He was previously awarded an MEng in Materials Science, also from the University of Manchester. His research looks into the physics of ink jet printing, in particular the processes of droplet deposition, coalescence and phase change from printable ink to functional material.