Direct ink-jet printing and low temperature conversion of conductive silver patterns

P. J. SMITH*, D.-Y. SHIN, J. E. STRINGER, B. DERBY
School of Materials, University of Manchester, Grosvenor Street, Manchester, MI 7HS, UK
E-mail: p.smith-2@manchester.ac.uk

N. REIS
Institute Superior Tecnico—ICEMS, Av. Rovisco Pais 1, Lisbon 1049-001, Portugal

Published online: 15 May 2006

A drop-on-demand ink-jet printer has been used in the production of conductive silver tracks onto glass, polyimide, polytetrafluoroethylene, carbon and glass fibre reinforced epoxy substrates. Silver patterns were obtained from an organometallic solution by heat treatment at 150°C in air and were found to have resistivity values of 1.3 to 2 times the theoretical resisitivity of bulk silver. Printed track lateral resolution is a function of the ink/substrate wetting behaviour and a simple model is presented that relates track width to equilibrium contact angle. The influence of printing parameters and substrate surface properties on line quality is discussed.

1. Introduction

In order to use ink-jet printing to deposit and form metallic conducting tracks on a range of substrates for electronic applications, it is necessary to develop a precursor ink that can be converted to a conductive deposit without damaging the substrate. If the conversion is carried out by the action of heat, then the associated local temperature increase must be as low as practically possible to avoid such damage. The use of inks containing an organometallic compound dissolved in a suitable carrier fluid offers such a route. The solvent used is usually volatile, which is advantageous as the carrier fluid evaporates after deposition [1, 2]. Organometallic inks containing copper [3], gold [4] and silver [5] have been printed and subsequently processed to obtain conductive tracks of the desired metal on a range of substrates. Silver-based inks are frequently used due to bulk silver having the lowest resistivity of all the elements [6]. 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 [7]. Conversion of organometallic inks to metal requires processing at relatively low temperatures, e.g. 180°C [5]. This processing temperature is lower than that reported as required for sintering silver nanoparticles in organic solvents [8, 9].

The ink-jet printer used for this study employed the drop-on-demand (DOD) technique, whereby the placing of droplets was achieved by mechanically positioning the print head directly above the desired location and generating said droplets when required. Droplet formation is initiated by applying a pressure pulse to an ink-filled chamber with a small opening. This action results in the ejection of a column of ink from the orifice and the subsequent formation of a droplet, due to surface tension. Inks must be formulated to fit the physical and rheological requirements of fluid flow in an ink-jet print head when extending ink-jet 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 print head generates satellites as well as the desired droplet [10].

One of the problems that have been observed when printing an organometallic ink onto a substrate is that the deposited line can display a morphological phenomenon commonly called ‘coffee staining’ [11]. Droplets and tracks that display this effect have a significant concentration of solute at their edges and in extreme cases no material remains in the centre. This occurs when the contact line (that is where the ink-air, ink-substrate and substrate-air interfaces meet) of the drying deposit is pinned and liquid evaporating from the edge has to be replenished by solution from the deposit’s interior. Cuk et al. [3] have observed that a greater uniformity of material is distributed across the width of a printed feature when solutions of increased concentration are used, which reduces the severity

*Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-6653-1

of coffee staining. Variation in line feature can also result as a consequence of the parameters utilised for printer operation. Vest et al. [12] observed an increase in line width and film thickness for higher frequencies and slower substrate speeds, as the mass deposition rate per unit length is seemingly increased.

In this paper, we report on the ink-jet printing of a commercially available ink that can be reduced to silver at temperatures as low as 150°C. This ink was originally developed for applications other than ink-jet printing. In order to allow it to be used successfully, it has been diluted to achieve the required viscosity. A number of substrates have been used and the variation in printed track width under the same nominal printing conditions has been investigated. This variation is correlated with the contact angle the ink forms for the given substrate and a simple relationship is proposed that provides an estimate of final track width for a printed track on a given substrate if the contact angle is known.

2. Experimental

The silver ink used in this study consisted of a silver organic compound dissolved in toluene (Product No. C2030325R11, Gwent Electronic Materials, Pontypool, Wales.) Thermogravimetric analysis, which employed a typical experimental thermal profile, was carried out on the ink and the result is shown in Fig. 1. The ink was first dried at room temperature for 2 hours in order to observe the mass loss due to the volatility of toluene; a value of 20% was seen. The ink was then heated at the rate of 1°C min^{-1}. The organic constituents of the ink were found to decompose at temperatures below 150°C leaving a metallic silver residue, which corresponded to an initial metal content of 14%.

Ink 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} (spindle SC4-18), using a temperature controlled small sample adapter. Surface tension was determined by the pendant drop method using conventional CCD imaging and dedicated image analysis software (Camtel FTA 200, Royston, UK). The viscosity and surface tension of the ink were 7 mPa · s and 26.3 mJ · m^{-2} respectively. Both of these values fall within the parameters specified by MicroFab, the print head manufacturers, and the ink was therefore deemed acceptable for printing [13].

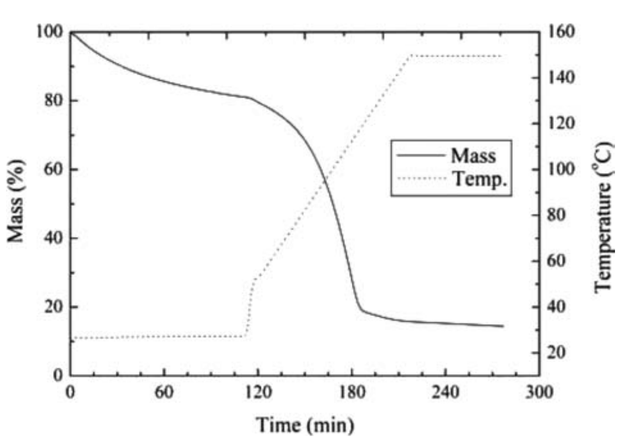

Figure 1 Thermo gravimetric analysis of the silver-containing ink.

Five different substrates were used to examine the effect of wetting characteristics on the lateral resolution of the printed patterns. These included: soda-lime glass (microscope slides, BDH, Poole, Dorset, UK), polyimide film, Kapton® (type 500 HPP-ST, Du Pont, Wilmington, DE, USA), Polytetrafluoroethylene (Teflon™, Du Pont, Wilmington, DE, USA) and both carbon and glass fibre reinforced epoxy composites (provided by BAE Systems, Bristol, UK). The contact angle that the sessile drop of the ink formed with different substrates was measured using image analysis software (FTA 200, Camtel, Royston, UK). In this technique, a droplet of ink was carefully placed upon a substrate and photographed. All substrates were cleaned with acetone prior to contact angle measurement.

The silver ink was tested using a 60-micron orifice diameter piezoelectric driven ink-jet print head (MJ-AB-01-60, MicroFab Technologies Inc., Piano, TX, USA). Jet driving parameters, such as frequency, voltage and the pulse duration of the trapezoidal electric pulses used to excite the piezoelectric transducer, were varied within the range obtainable by the printing platform driver electronics.

Printing experiments were performed using a single print head mounted on the carriage of a *XYZ* platform, (RTM, Sanders Design International, Wilton, NH, USA) which enabled full movement in the *XY* plane. Tracks were obtained by synchronous drop ejection and translational movement, so-called vector drawing or plotting. All printing was performed at room temperature on substrates cleaned with acetone. The printed tracks were allowed to dry at room temperature for 10 minutes before being placed in a temperature controlled muffle furnace, set at 150°C for 60 min, in order to reduce the ink to silver.

The resistance of a number of the printed circuits was measured using a four-point probe technique allowing resistivites, based on track dimensional data, to be calculated. The as-processed samples were characterised by optical microscopy and scanning electron microscopy – SEM (6300 SEM, JEOL, Tokyo, Japan) to determine the morphology and dimensions of the printed tracks. Track dimensions were also obtained by phase contrast microscopy – PCM (MicroXAM, ADE Phase Shift, Tuscon, AZ, USA), in the case of the silver tracks printed on glass.

The as-printed track width (w) can be estimated using a simple relationship. It is assumed that if the contact angle of the ink on a substrate is low, the track will adopt a cylindrical cap shape (Fig. 2). In this case, mass conservation gives:

$$\frac{\pi d^3}{6} N = \left(r^2 \theta - \frac{wr \cos \theta}{2} \right) L, \qquad (1)$$

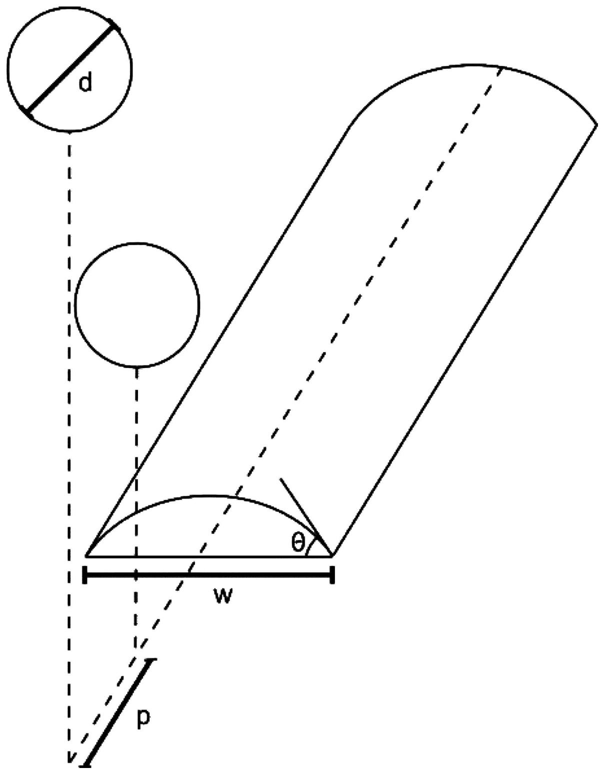

Figure 2 Diagram showing the theoretical assumptions made in modelling the relationship between final track width and contact angle.

where d is the drop diameter, θ is the contact angle, r is the radius of the cap, N is the number of droplets printed for a track of length L. Rearranging Eq. 1 and substituting for r results in:

$$w^2 = \frac{\dfrac{\pi d^3}{6p}}{\dfrac{\theta}{4\sin^2\theta} - \dfrac{\cos\theta}{4\sin\theta}}, \tag{2}$$

where p is the spacing of adjacent droplets or the "dot-pitch" (L/N).

3. Results and discussion

Fig. 3 shows the images of forming droplets, demonstrating that both the droplet size and the velocity (i.e. the separation between droplets at fixed frequency) can be modulated in order to control the mass deposition rate and hence the track's final width and thickness, as observed by Vest et al. [12]. This is further illustrated in Fig. 4, which shows the influence of pulse amplitude, (ΔV) on drop mass and velocity. The behaviour of drop properties on printing parameters and fluid physical properties has been reported in detail elsewhere [10].

Fig. 5 shows a montage composed from images of the same complex circuit patterned on three different substrates; all of which were heat treated in a muffle furnace at 150°C for 60 minutes in air. It can be seen that discrete, continuous lines are formed on each substrate. The average widths formed by the silver tracks on the five substrates were measured using optical microscopy and are shown in Table I.

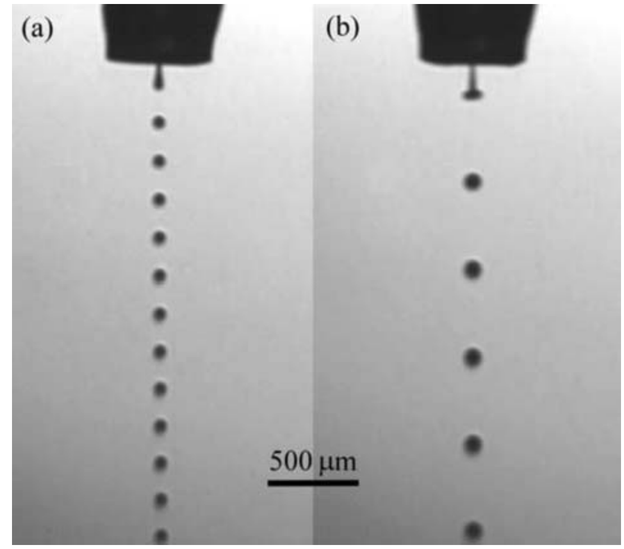

Figure 3 Stroboscopic imaging of the silver ink droplet streams obtained at different driving parameters: (a) frequency = 6 kHz, pulse duration = 45 μs, $\Delta V = 50$ V; (b) frequency = 6 kHz, pulse duration = 13 μs, $\Delta V = 70$ V.

Some variation in track width is evident on each of the substrate materials. This is believed to come from two sources. Firstly, the track width is controlled by the contact angle on the surface and this in turn depends on the substrate's surface energy and surface roughness. It is possible that there is some variation in the surface energy across a given specimen; although the substrates were cleaned with solvent prior to each experiment. The tracks printed onto the substrates made from fibre reinforced materials exhibited variations consistent with roughness arising from their weaving patterns. Secondly, it is possible that there are variations in ink droplet size during deposition. The printer is designed to maintain a uniform drop spacing on the surface (dot pitch) by relating drop generation frequency to the translational speed of the print head in the $x-y$ plane. It is known that the volume and velocity of an ink-jet printed drop, formed from the

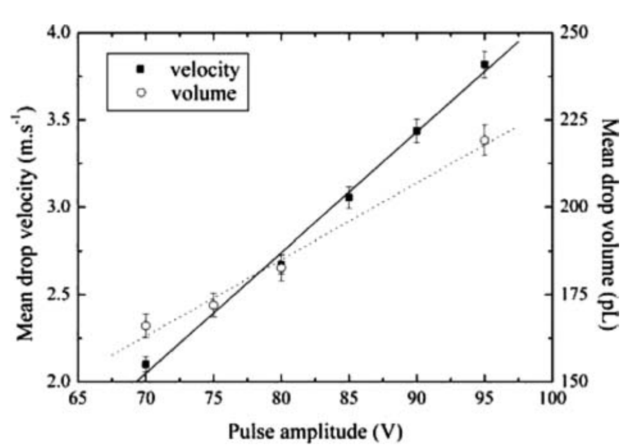

Figure 4 Drop volume and velocity as a function of piezoelectric excitation voltage, with linear regression coefficients of 0.994 for volume and 0.997 for velocity.

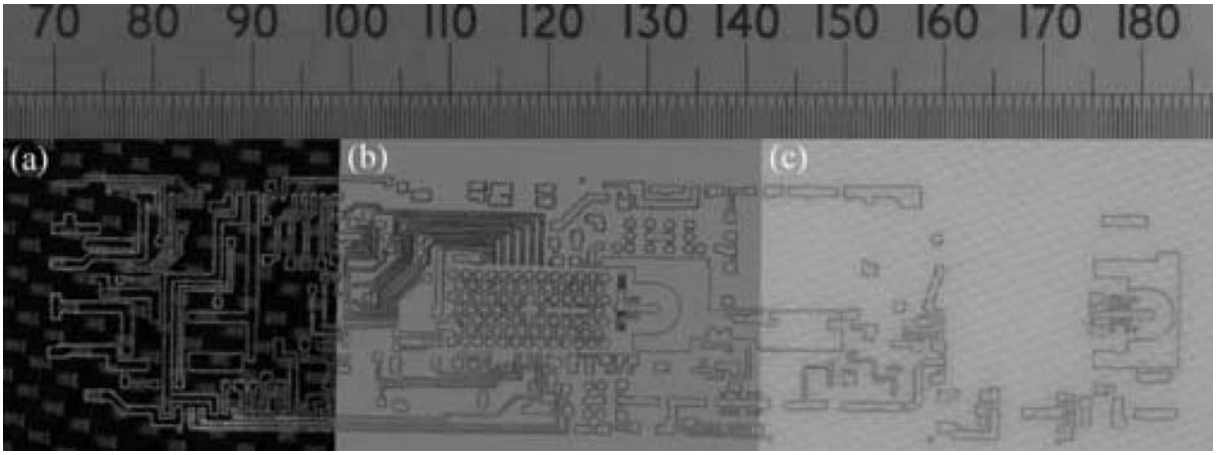

Figure 5 A photographic montage showing the same circuit printed on (a) CFRP, (b) polyimide and (c) GFRP. The length divisions shown on the ruler are millimetres.

design of DOD printhead used in this study, is a function of driving frequency [14, 15]. Thus when the print head accelerates or decelerates, (at the beginning and the end of each drawing vector respectively), there may be variation in drop volume and hence final track width.

Initial measurements showed that the substrate used had a significant influence on mean track width. From Table I, it can be seen that there is a strong correlation between increasing line width and decreasing contact angle of the ink on a given surface. The measured final track widths from Table I were plotted, and compared to a line calculated from Eq. 2 using contact angle data, θ, as shown in Fig. 6. The agreement between the predicted line width and the measured values is reasonable. Note that the line width has been measured after drying and heat treatment. Thus the line width would be expected to be smaller than that predicted by Eq. 2. However, about 86% of the ink's mass is removed during drying and conversion to silver and thus the line width retraction would be expected to be greater than observed. From this observation, we conclude that the fluid must be pinned by the initial contact line for so little droplet retraction to have occurred on conversion to silver.

TABLE I. Printed silver track widths and the contact angle that the silver ink formed with the substrate

Substrate	Track Width (μm)	Contact Angle (°)
Teflon™	82 ± 8	58.7 ± 2.1
GFRP	138 ± 11	32.9 ± 1.4
Kapton™	204 ± 15	11.1 ± 3.1
CFRP	238 ± 13	17.7 ± 2.1
Glass	358 ± 26	5.9 ± 1.8

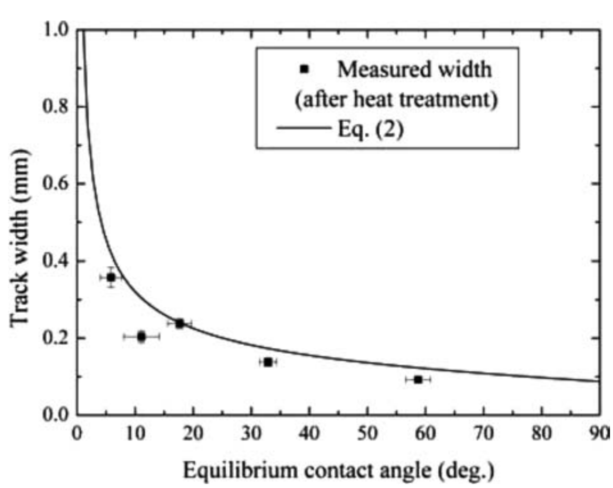

Figure 6 A graph showing the relationship between contact angle and final track width. Each data point corresponds to a different substrate.

The silver tracks were examined by SEM in order to determine microstructural features after heat treatment. The micrograph shown in Fig. 7 is a typical exampl silver track. The track has a granular appearance and on higher magnification, it is si be nano-crystalline with a mean grain size of approximately 200 nm. There are few voids and an even coating has formed as a result of the deposition and heat treatment process. The inset, showing a high-resolution SEM image of these silver grains, demonstrates their dense packing and narrow size distribution. The fine grain size is thought to be consistent with the low conversion temperature (150°C), which would introduce multiple nucleation events. The rapid evaporation of solvent would also limit mobility of silver, therefore resulting in localised crystal growth within the forming track microstructure.

The tracks printed on glass were examined using PCM. Fig. 8 shows a typical three-dimensional profile constructed from the data obtained. Cross-sectional areas have been plotted from this data and used to determine values for resistivity. The edges of the track show a distinct 'ridge'. This feature is due to the so-called 'coffee stain' effect that occurs during the drying of dilute solutions or particle dispersions first described by Deegan et al. [11]. Deegan hypothesised that the edge of a spreading droplet is pinned on the substrate. Although the concentration of solute in the initial droplet is uniformly distributed, preferential evaporation of solvent near the edges (contact line)

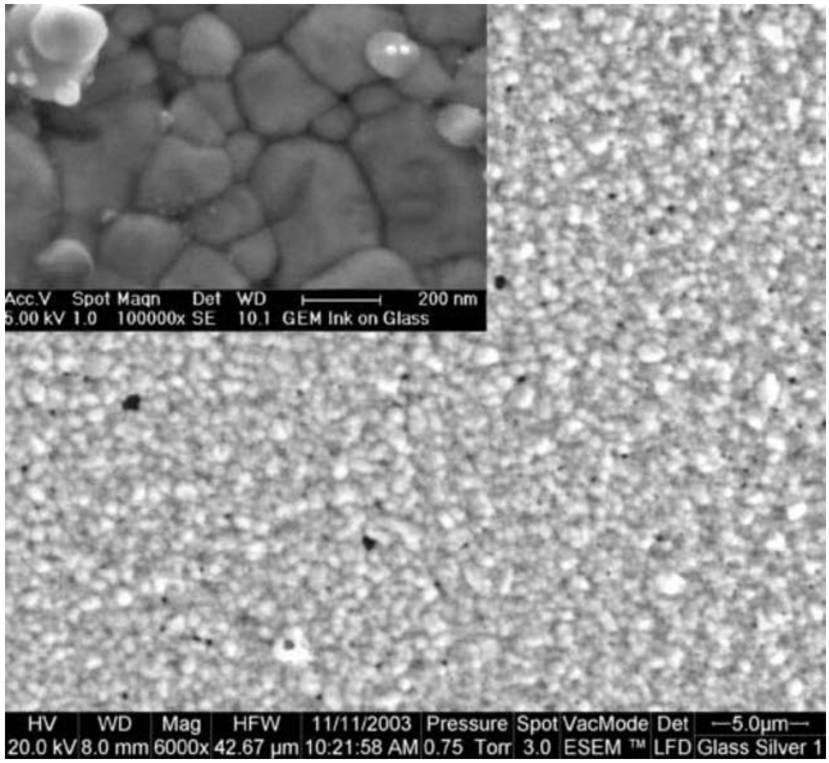

Figure 7 The microstructural detail of the silver ink printed on glass.

causes an inhomogeneous distribution of solute due to convective flow. A net flow is established that brings material from the centre and deposits it at the pinned droplet edge. Fig. 8 shows a weak concentration of material towards the track edges and represents a mild 'coffee-stain'. This is due to the high concentration of solute used and has also been observed for tracks printed using solutions of copper hexanoate in chloroform [3].

A mean resistance figure of 162 ± 81 Ω/m was obtained using the four-way contact probe technique for track lengths of 10 cm on all substrates. Making use of the cross-sectional data obtained by PCM, (Fig. 8) and integrating the acquired profiles, the cross-sectional area of the tracks printed on glass and polyimide was measured as $1.25 \pm 0.25 \times 10^{-10}$ m^2 after heat treatment. From this the resistivity of the printed silver is in the range $2\text{–}3 \times 10^{-8}\ \Omega \cdot \text{m}$, which corresponds to 1.3 to 2 times the resisitivity of bulk silver ($1.6 \times 10^{-8}\ \Omega \cdot \text{m}$).

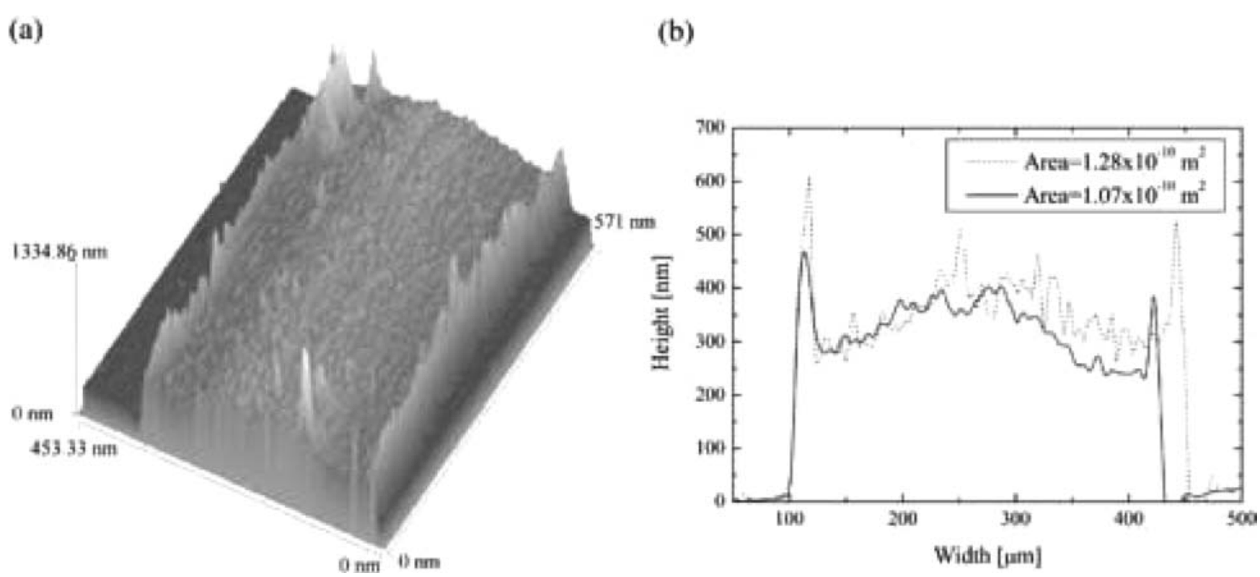

Figure 8 Three-dimensional profile and two cross sections of a silver track on glass obtained using PCM.

4. Conclusion

A silver-containing organometallic ink has been printed onto a range of substrates at room temperature using a drop-on-demand ink-jet printer. These tracks were then thermally processed at temperatures as low as 150°C. The calculated resisitivity was found to be 1.3 to 2 times that of bulk silver. The low heat treating temperatures achieved allow the use of the technology with a wide variety of substrates, notably, polymeric media. It was found that final track width correlates well with predictions of as-printed width as a function of equilibrium contact angle and printing variables such as drop size and adjacent droplet spacing.

Acknowledgements

The authors would like to thank the EPSRC for their financial support, BAE Systems for the provision of the carbon fibre and glass fibre epoxy resin substrates. NR would like to acknowledge the Portuguese Foundation for Science and Technology for his post-doctoral research fellowship (BPD/2001/7112).

References

1. K. F. TENG and R. W. VEST, *IEEE T. Compon. Hybr.* **11** (1988) 291.
2. K. F. TENG and R. W. VEST, *IEEE T. Compon. Hybr.* **10** (1987) 545.
3. T. CUK, S. M. TROIAN, C. M. HONG and S. WAGNER, *Appl. Phys. Lett.* **77** (2000) 2063.
4. S. MOLESA, D. R. REDINGER, D. C. HUANG and V. SUBRAMANIAN, *Mat. Res. Soc. Symp. Proc.* **769** (2003) H8.3.1.
5. T. KAYDANOVA, A. MIEDANER, C. CURTIS, J. PERKINS, J. ALLEMAN and D. GINLEY, in Proceedings of the National Centre for Photovoltaics and Solar Program Review Meeting (Denver, Colorado, March 2003).
6. D. R. LIDE (Eds.) in Handbook of Chemistry and Physics, 77th edn. (Boca Raton, CRC press, 1996) p. 12.
7. R. W. VEST, in Ceramic Films and Coatings Chapter 9, edited by J. B. Wachtman and R. A. Haber (William Andrew Publishing/Noyes, 1993) p. 303.
8. S. B. FULLER, E. J. WILHELM and J. M. JACOBSON, *J. Microelectromech. S.* **11**(1) (2002) 54.
9. J. B. SZCZECH, C. M. MEGARIDIS, D. R. GAMOTA and J. ZHANG, *IEEE T. Electron. Pack.* **25** (2002) 26.
10. N. REIS, C. AINSLEY and B. DERBY, *J. Appl. Phys.* (in press).
11. R. D. DEEGAN, O. BAKAJIN, T. F. DUPONT, G. HUBER, S. R. NAGEL and T. A. WITTEN, *Nature* **389** (1997) 827.
12. R. W. VEST, E. P. TWEEDELL and R. C. BUCHANAN, *Int. J. Hybrid Microelectron.* **6** (1983) 261.
13. http://www.microfab.com/equipment/pdf/MicroJet_Dev_Spec.pdf (last accessed on the 16th February 2005).
14. J. F. DIJKSMAN, *J. Fluid. Mech.* **139** (1984) 173.
15. N. REIS and B. DERBY, *Mater. Res. Soc. Symp. Proc.* **624** (2000) 65.

Received 28 July
and accepted 14 September 2005