Low Curing Temperature Silver Patterns from Soluble Inks

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Abstract

Silver neodecanoate salt is both light and heat sensitive, and is suitable for inkjet printing when dissolved in organic solvents. We have studied the electrical properties of inkjet printed silver samples, derived from silver neodecanoate ink, and investigated the influence of ultra violet light (UV) treatment on the silver samples before air oven cured at variety length of time. In addition we have studied the influence of thermal pre-treatment on the printed samples. Thermally cured printed silver squares show minimum resistivity of approximately 3x bulk silver. The microstructure shows an interconnected network of silver nanoparticles after curing. The resistance of the printed pads are shown to relate to the connectivity of the resulting sintered nanoparticle network as measured by the ratio of the sintered neck diameter to the original particle diameter.

Introduction

Silver nanoparticle suspension ink and silver organometallic solution ink are two widely used silver inks as a method for printing electrical conducting patterns for inkjet printing (IJP) [1-4]. Solution based inks have advantages in being more stable against segregation or settling in storage. Both routes can lead to relatively low resistivity silver patterns after low temperature thermal treatment compatible with flexible substrates. Silver neodecanoate ink has been considered in a previous study as a good precursor to be used in IJP [1].

Experimental Method

Commercial silver neodeconoate ink was purchased and characterized. Printing experiments were undertaken using Dimatix Materials Printer DMP 2800 (FujiFilm Dimatix, Santa Clara, CA, USA). 10 x 10 mm arrays of isolated dots and continuous pads were printed onto glass substrates (Menzel-Glaser, Menzel GmbH + Co KG, Saarbrucken, Germany). Samples were dried in ambient conditions and stored in darkness. Prior to thermal curing, some of the samples were exposed to UV radiation with peak intensity at 355 nm wavelength (ProCure UV Finisher, 3D Systems, SC, USA). The height of the printed deposits was measured by white light interferometery (PCM MicroXAM-100, ADE Phase Shift, East Hampton, CT, USA). The conductivity of the films was tested using the four probe technique (Jandel Multiposition Wafer Probe, RM3-AR, Jandel, Linslade, UK). Microstructures of the silver deposits after curing were investigated by scanning electron microscopy (SEM), (XL30 FEG-SEM, FEI, Eindhoven, Netherland).

Results and Discussion

Influence of UV and Thermal Cure on Printed Deposit

An array of isolated silver neodecanoate dots were dried under ambient condition in the darkness and were exposed to UV light for various times. The height of the droplets was measured by white light interferometry after 30 minutes exposure before exposing for further 30 minute intervals. As the UV exposure time was increased the height of printed dots reduced dramatically. In the first 90 minutes, the height reduction per 30 minutes exposure was fairly constant. After 120 minutes exposure there was a sudden drop in thickness followed by little further reduction with further exposure to UV radiation (figure 1). Irrespective of the heat generated by the UV radiation, the height of a fully oven cured single printed drop is about 70 nm.

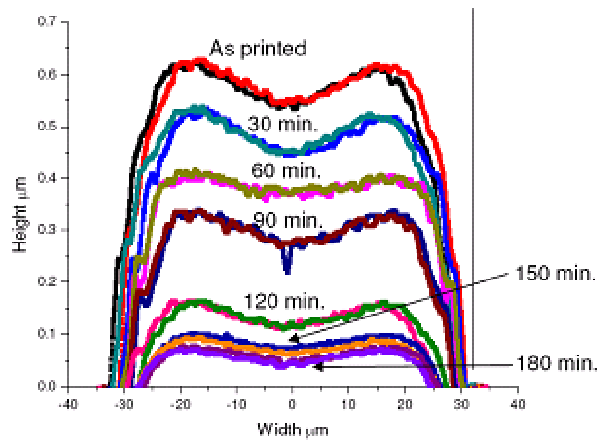

Figure 1. *Height and width of individual printed drops (data from 2 drops shown) after drying and then exposed to UV radiation for varying exposure times.*

Film Electrical properties and Microstructure

The electrical properties of the printed and cured silver pads are strongly influenced by the temperature of the thermal cure. Figure 2 shows that the printed film resistivity is reduced to approximately 3x bulk silver after 30 minutes exposure to 200 °C. This temperature is too high for use with most flexible substrates; however cure at 160 °C results in resistivity < 10 x bulk values. Curing at 140 °C produced a film with a very high resistivity and is not shown on the plot.

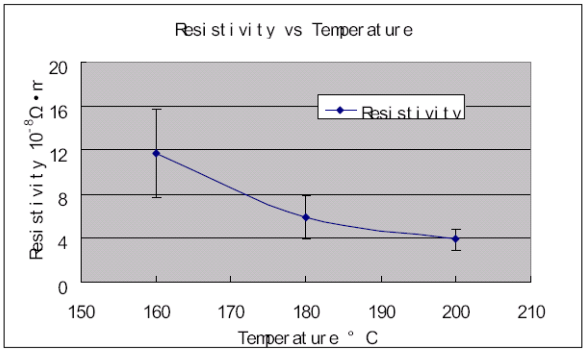

Figure 2. *Electrical resistivity of printed and cured silver films as a function of curing temperature*

Cured silver printed pads were examined by SEM to study the evolution of their microstructure (figure 3). At the lowest curing temperature of 140 °C the silver film is seen to contain a large number of isolated silver nanoparticles with mean diameter around 50 nm with little discernible neck formation between adjacent particles. In figure 3b we can see that after curing at 160 °C there is more evidence of particle-particle interactions and a continuous conducting network is formed. Comparing the 160ºC and 180ºC samples (figures 3b and 3c), more connections are formed between the nanoparticles at higher curing temperature. It is also noticeable that the higher curing temperature results in a lower fraction of voids in the structure.

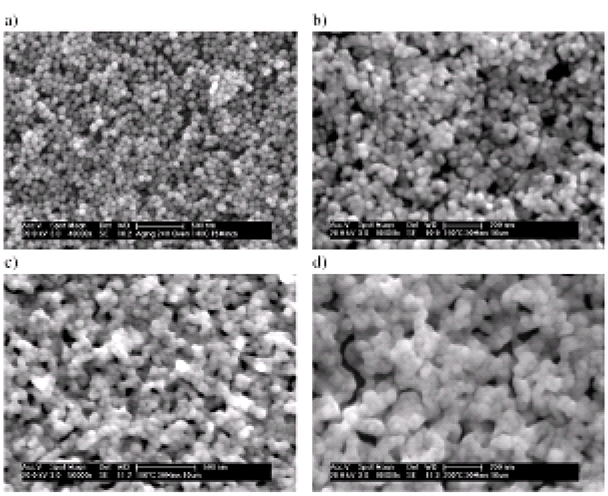

Figure 3. *SEM micrographs showing the microstructure of the printed silver thin films after curing for 30 minutes at elevated temperature: a) cured at 140 °C, b) cured at 160 °C, c) cured at 180 °C, d) cured at 200 °C*

The sample cured at 200ºC for 30 minutes (figure 3d) shows significant sintering of the original nanoparticles to form larger structural units and lowest residual porosity. The 'neck ratio', the ratio of the mean length of connection between adjacent silver nanoparticles (the neck) against the mean diameter of the nanoparticles, was calculated and the influence on this measure of nanoparticle connectivity studied.

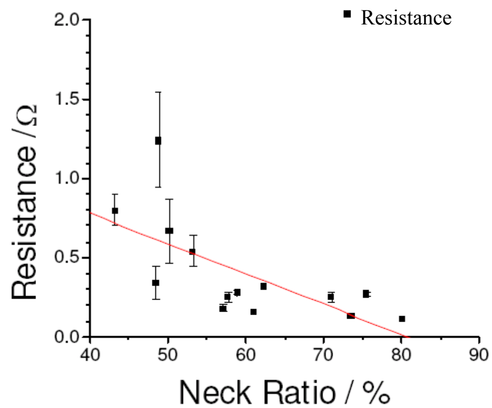

Figure 4. *Resistance of the printed silver pads as a function of neck ratio*

In Figure 4 the 4-point probe data shows a clear trend with pad resistance decreasing steadily as the neck ratio increases. However, because of difficulties in measuring an accurate film thickness for the printed pads between the probe sites, trend in the measured resistivity is less clear (figure 5).

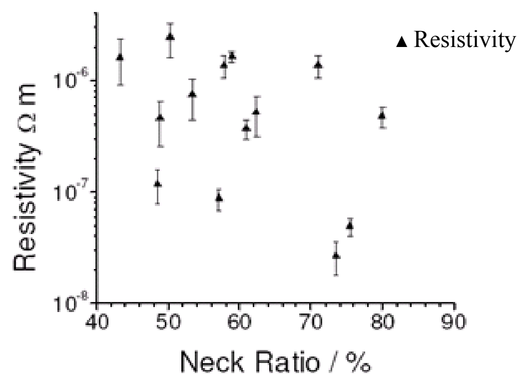

Figure 5. *Resistivity of the printed silver pads as a function of neck ratio*

Conclusions

Silver neodecanoate soluble ink provides a viable low temperature curing route for inkjet printing conducting tracks on flexible substrates. Track shape is controlled by the interaction of the first printed layer with the substrate. Subsequent printing passes do not change the width of any printed feature but increase its height. In addition it was found that the sequence of printing and curing had no effect on track dimensions. Sintered tracks do not reach full density under practical conditions but the resistivity of samples can reach an acceptable level with low temperature curing. Track resistivity scales with connectivity of the microstructure. Optical (UV) curing produces denser tracks, which may lead to lower thermal treatments but this needs further study.

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Author Biography

Bojun graduated from Fudan University, China in 2005 and gained his MSc in Advanced Engineering Materials from University of Manchester in 2006. His MSc dissertation concerned the extrusion of chitosan and alginate gel for biomedical applications. He decided to continue his research in rapid prototyping at the University of Manchester to study for a PhD. He is currently in his final year researching in the field of inkjet printing and direct writing of electronics.