Conductive Copper and Nickel Lines via Reactive Inkjet Printing

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Abstract

Conductive copper lines were directly written on paper through inkjet printing of a copper salt and a reducing agent sequentially from a multi-color printhead. The copper ink was an aqueous copper citrate solution and the reducing agent was a solution of sodium borohydride (NaBH4). The two inks were loaded in two separate compartments of a traditional HP color cartridge, which enabled the generation of two droplet streams from the two separate compartments. The cartridge was fixed above an X-Y positioning table and conductive copper lines prepared using multiple printing passes. The estimated conductivity obtained on paper (1.8 ´ 106 S·m-1), is about 1/30 that of bulk metal copper (59.6 ´ 106 S·m-1 at room temperature). Oxidation of the printed copper lines was studied using EDS elemental analysis of lines printed onto polyvinylidenefluoride (PVDF) membranes. The Cu/O ratio of copper lines decreased over 400 hours in air, due to oxidation, but leveled off afterwards. The same approach has also been applied to the printing of nickel where oxidation is less marked.

Introduction

Many groups are developing the technology to print low-cost flexible electronics for a wide range of applications [1,2]. As with conventional electronics, these applications will need logic, displays, power supplies and sensors. Methods are thus needed to print luminescent materials, semiconductors, dielectrics and conductors. Most conventional printing methods have been proposed for printed electronics. As a non-contact process, inkjet printing has advantages for multilayer circuits and pilot roll-to-roll inkjet systems have been tested.

Currently the favored inkjet printable conductor is silver, printed as a nanoparticle ink which is then sintered at a temperature low enough to avoid destroying the substrate [3,4]. An alternative to nanoparticle silver ink is to print silver salt and a reducing agent sequentially. This has been demonstrated using a combination of silver nitrate and ascorbic acid [5,6]. It is also possible to define a pattern for electroless plating by printing a line of metal "seeds" and then putting the substrate into an electroless plating solution, which we have demonstrated for silver lines printed onto textiles [7].

While silver nanoparticle inks do give excellent conductivity, the production process for the nanoparticles makes the inks very expensive. Printed copper is a desirable alternative but copper nanoparticles are rapidly oxidized in air so that a more complex printing, reduction and sintering process would be needed. Sintering would probably have to be done in a reducing atmosphere. Larger particles would be stable but would settle in the ink and would sinter only at high temperatures. Bidoki et al. point out that patents do describe two-ink inkjet printing of copper in principle but found that this did not work in practice due to oxidation. Copper lines have been inkjet printed by printing palladium seeds followed by electroless plating [8].

The choice of substrate is also important. For many studies with silver nanoparticle inks, polyester film is the chosen substrate but polyimide may be used if a sintering temperature over 120^{o}C is needed. It is also necessary to control the wetting properties of the film to prevent spreading of the lines during printing. Since adhesion between the substrate and metal must always be a concern, we have worked exclusively with porous substrates such as paper, textiles and membranes. In this case the substrate can act as a reservoir for the printed reagents prior to reaction and can reinforce the weak, partly-sintered metal during flexing. Ultimately we would expect that porous materials would be designed specifically for printed electronics.

In this paper we describe the successful printing of copper lines onto paper by a two-component reduction process similar to an electroless plating process. The typical composition of an electroless copper-plating bath consists of a copper salt, a complexing agent, a reducing agent and a pH adjustor. On contact with the plating solution, metal nanoparticles on the substrate catalyze reduction of the copper ions to metal [9]. Reducing agents used for electroless plating include formaldehyde [10,11,12], $NaBH_4$ [13,14], sodium hypophosphite (NaH_2PO_2) [15, 16,17,18,19], glyoxylic acid [20,21], and amine borane [22]. In our work, inkjet printing droplets of copper citrate and $NaBH_4$ simultaneously onto paper allows direct reduction on the substrate to form metallic copper lines. To illustrate that this approach can be extended to other conducting metals, we also describe the printing of nickel conductors.

Experimental

Materials.

Copper sulfate (CuSO4), nickel sulfate (NiSO4), sodium citrate, and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich (St. Louis, MO). Sodium hydroxide (NaOH) was purchased from Fisher Scientific (Pittsburgh, PA). All the agents were used without further treatment. Photocopy paper (20 lb weight, acid-free bright paper) was cut into desired size and used as the substrates in this study unless otherwise indicated. To provide an oxygen-free substrate for elemental analysis, poly(vinylidenefluoride) (PVDF) membranes with 0.45 µm pore size (Durapore, Millipore) were used. A 4 % (v/v) solution of Trycol 5952 (an ethoxylated isodecyl alcohol, Cognis, Cincinnati, OH) was used as the wetting agent for treatment of the PVDF membranes.

Ink Preparation

$CuSO_4$ and sodium citrate powders were dissolved in distilled water to form the copper ink of concentrations up to 1.25M.

Citrate is a copper chelator that increases the solubility of the copper and the stability of the solutions. For the reducing ink, $NaBH_4$ was dissolved in 0.5 M NaOH solution (pH 14). The high pH stabilizes the $NaBH_4$. For nickel line printing, 2.5 M aqueous $NiSO_4$ solution was prepared as the nickel ink and 1.25 M $NaBH_4$ was used as reducing ink.

Inkjet Printing

Hewlett-Packard HP 49 color cartridges were emptied, rinsed thoroughly with distilled water, and used for the inkjet printing. The typical droplet size from such cartridges is 15 pL, corresponding to a 30 micron drop diameter. An MD-2 dual step motor driver system (Arrick Robotics, Tyler, TX) was connected with a computer-controlled X-Y positioning table (Velmex, Bloomfield NY). The color cartridge was held by a cartridge holder (removed from an HP color printer) and mounted above the X-Y table onto which paper substrate was placed for printing. Current pulses were provided to selected nozzles using a home-built system developed from descriptions published by HP [23]. A program was written to control the movement of the X-Y table at a defined angle to the lines of nozzles on the cartridge base, so that the printing streams from two nozzles in different color sections of the cartridge were superposed, to form one single printed line. Droplets were pulsed at rates from 250-1000 Hz with the table moving at speeds of 2.2 and 4.4 mm/sec, giving different degrees of saturation during a single printing cycle. The system cycled, back and forth, over the same line path for up to 400 times (cycles) to build a thick copper layer.

Characterization and Analysis of Printed Copper Lines

A Nikon Ellipse L 200 optical microscope and a JEOL JSM-5610 scanning electron microscope (SEM) were used to examine the appearance and morphology of the inkjet printed copper and nickel lines. An energy dispersive X-ray spectrometer (EDS) coupled with the SEM was used to conduct the elemental analysis for printed copper lines exposed to air for different times.

In the EDS study of the oxidation of printed copper lines, PVDF membranes were used as the substrate, since, unlike cellulose, they give no substrate oxygen signal. Membranes were treated with a 4 % (v/v) aqueous solution of Trycol 5952 before the inkjet printing. Copper lines printed on treated PVDF membranes were washed repeatedly with distilled water and then dried in vacuum or in an oven at 60 ºC for 2 hours. The samples were then exposed to air and subjected to EDS analysis at different exposure time to obtain the Cu/O ratios.

A two-probe method was used to measure the resistance of the inkjet printed copper lines. Conductive silver (Ag) paint was used to draw lines across the copper to form 5 mm line sections for the resistance measurement.

Results

Figure 1 shows copper with a nodular morphology printed onto paper. A major concern with printing copper by this method

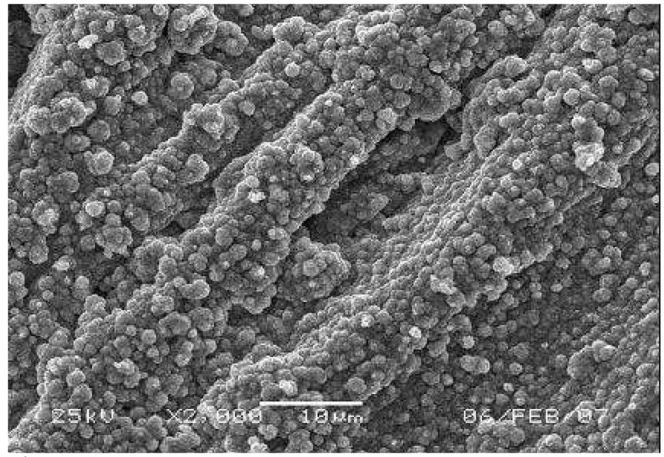

Figure 1*: Copper printed onto paper, 350 cycles of copper solution and reducing agent.*

or from nanoparticles is that oxidation can occur resulting in a non-conducting layer. For films printed onto paper we were not able to find an analytical method to distinguish between copper oxide and oxygen in the substrate. Accordingly films were printed onto an (oxygen-free) PVDF membrane where, as shown in figure 2, the copper to oxygen ratio in the film can be determined. The oxygen content decreases as the printed layer becomes thicker.

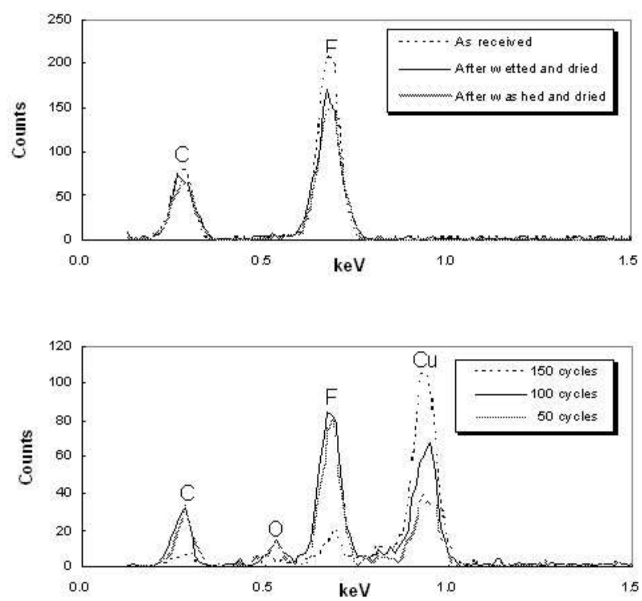

Figure 2. *EDS of films printed onto PVDF membrane showing low oxidation level of copper. Top membrane only, bottom with printed copper film of varying thickness.*

As shown in figure 3, the thinner layers become almost fully oxidized to Cu_2O during deposition. Thicker layers become stable after some initial oxidation. As shown in figure 1, the films have a very nodular morphology are probably essentially particulate untila substantial thickness is built up.

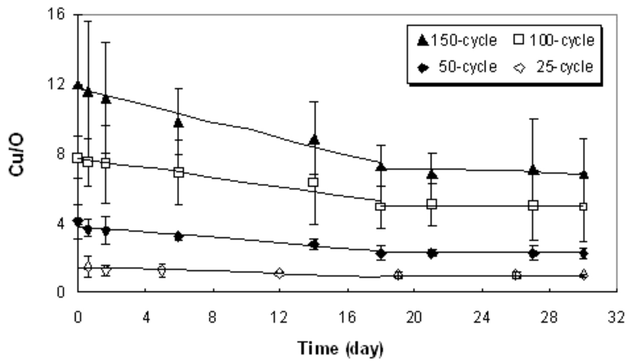

Figure 3. *Copper to oxygen ratios for different films thicknesses as printed and as aged over 1 month. A ratio of 2:1 corresponds to 100% Cu_2O, higher ratios are mixtures of copper and oxide.*

In figure 4, the resistance of the thinner films starts high and then increases further on oxidation. In the thicker films the oxidation is limited to the surface and has little effect on resistance. Other work has shown that oxidation of copper follows a square root law and slows with time as expected for a diffusional process [24].

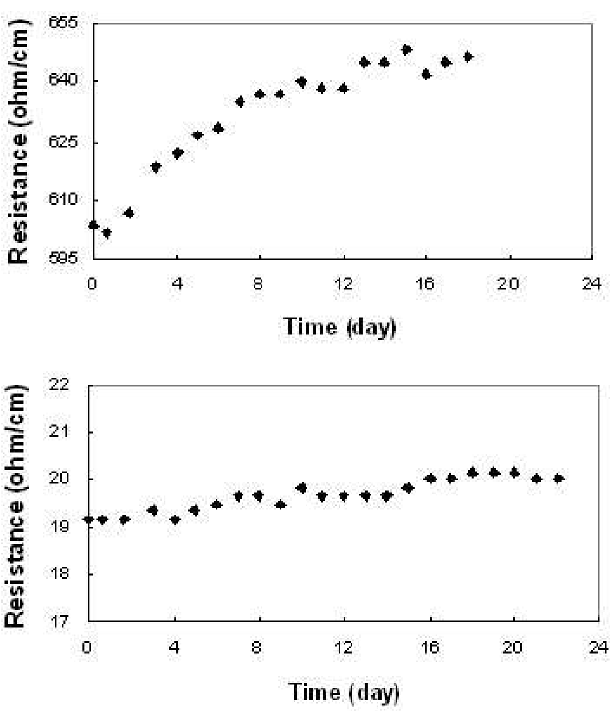

Figure 4. *Resistance of printed lines of copper versus oxidation time in air. Top 50 layers, bottom 150 layers.*

Nickel can be printed by a similar reductive route but is not sensitive to re-oxidation. Figure 5 demonstrated that conductivity of printed nickel films does decrease with the number of printed cycles as with copper but does not change significantly on air exposure.

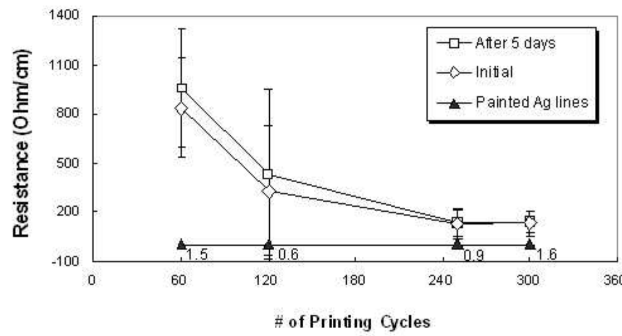

Figure 5 *Resistance of printed nickel lines as printed and after storage in air.*

Conclusions

We have developed a reactive inkjet printing process and demonstrated that conductive copper and nickel lines can be readily onto paper via such process. The best conductivity of printed copper lines is 1.8 ´ 106 S·m-1 and that of nickel is 2.2 × 104 S·m-1, about 1/30 and 1/600 of their bulk metal counterparts, respectively. Oxidation of the printed copper lines in air was studied using EDS elemental analysis of lines printed onto PVDF membranes as the substrates, and the results indicated that Cu/O ratio of lines printed for different numbers of cycles kept decreasing for about 400 hours and leveled off afterwards. Oxidation of inkjet printed nickel lines appears to be less severe.

The inkjet printing process could be applied to many other metals and to other types of materials formed by chemical reaction on substrates. In a practical application, some consideration would need to be given to removal of salt by-products by washing. It would also be advantageous to reduce the number of printing cycles by increasing the dissolved concentrations of reagents.

The inkjet printing process developed in this study may provide a promising method for patterned metallization of copper for fabrication of flexible electronics. We envisage that any production system would work on a roll-to-roll basis with multiple printheads.

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Author Biography

Paul Calvert was educated as a materials scientist at Cambridge and MIT and has been on the faculty at the University of Sussex, University of Arizona and UMass Dartmouth. He has worked on polymer crystallization and stabilization, composites and ceramics, biomimetic materials, rapid prototyping and inkjet printing.