Processing Thick-Film Screen Printed Metalon® CuO Reduction Ink with PulseForge® Tools

Vahid Akhavan, Kurt Schroder, Dave Pope, Stan Farnsworth*
NovaCentrix®
200-B Parker Dr, Suite 580, Austin, TX 78758, Phone: +1-512-491-9500
*Corresponding Author: stan.farnsworth@novacentrix.com

Introduction

Copper-based inks continue to be of great interest in the electronics community, as a lower-cost alternative to silver currently used. Recognizing that while not all copper inks are truly a cost-effective replacement for silver, one low-cost product currently available is the Metalon ICI-series of CuO inks. These inks are converted with PulseForge photonic curing tools from copper oxide to copper on low cost, flexible, and temperature sensitive substrates. This paper reviews details of successful application of these thick-film screen printed copper reduction inks, including the conversion to copper through photonic curing. Photonic curing is a transient process that can heat the deposited circuit to very high temperatures without heating and damaging the underlying substrate. Screen printing is used to produce patterns of the Metalon ICI-series CuO ink greater than 10 µm thick on paper substrates. The printed oxide patterns are converted to conductive copper circuits using composite pulses on the PulseForge system. Sheet resistances as low as 11 mΩ/sq were achieved. Here we demonstrate that the lower circuit resistance enables much higher current carrying capacity, which is important for a wide range of active systems. Currents as high as 1.4 A can be carried through a $^{1}/_{16}$" wide print that was deposited as an approximately 50 µm thick layer of CuO.

Background

Photonic curing has become an established processing technique widely used for processing high-temperature materials on low-temperature substrates, using microsecond-scale pulsed light from flashlamps.[1-6] The printed electronics industry is turning from traditional thermal processing to using photonic curing to process conductive inks, including of nanocrystal materials, on temperature sensitive substrates like paper, plastic, or fabric.[7-9] Also recognizing that not all curing equipment is comparable in capability, we will show how the PulseForge tools are used to deliver the necessary pulse power, energy, and architecture to effectively cure deep into the printed circuits. Specifically, recent work has shown that a composite (segmented) pulse structure, as depicted in Figure 1, is much better at achieving greater cure depth of thick-film printed circuits than a conventional square pulse structure.[10] Delivering such a pulse structure with the necessary power and energy levels was not possible without the innovation and the technology built into the PulseForge tools.[1-2]

The PulseForge tools are able to turn on and off the lamps over very short time scales, creating pulses as short as 25 μs, and as close together as 20 μs. These fast modulation times are used to create better drying response in thick-film materials, such as those produced with screen printing. The authors have determined that the pulse shaping capability, when combined with high power delivery, enable optimization of the pulse condition to enhance the desired reactions through thermal control of the system. This is especially true for processing depositions which are greater than 10 μm thick, such as from screen printing.

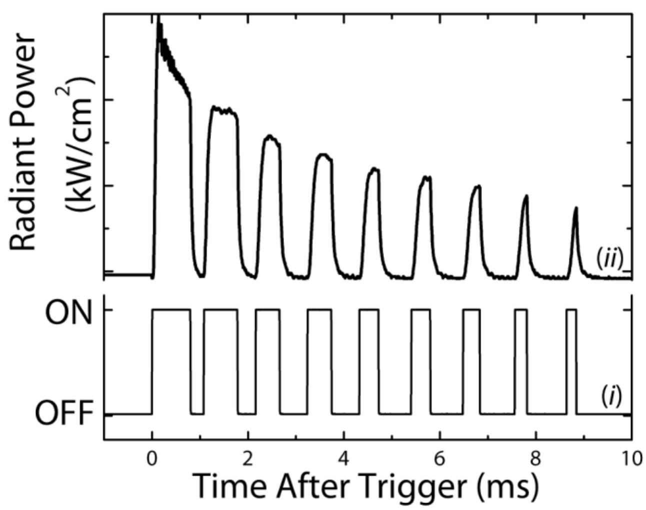

Figure 1: Illustration of (i) current through the switch and (ii) the resulting radiant power output from the flash lamp for a composite pulse.

Metalon ICI-series CuO reduction inks differ fundamentally from conventional Cu inks.[9] Because the CuO inks are based entirely on the use of copper oxide, the ink is already at its lowest oxidation state and is therefore completely stable under ambient conditions. In contrast, inks based on copper nanoparticles will degrade over time due to the oxidation of the Cu or require special handling and storage. The CuO inks are also based on the use of water, in contrast to organic solvents used in other copper inks. The CuO inks can also be processed in open air, in ambient room conditions, and do not require the use of reduction or inert atmospheres.

Methods

Metalon ICI-021 CuO reduction ink was screen printed in a 115 square pattern (7 $^{1}/_{8}$" long and $^{1}/_{16}$" wide) on bright white copy paper (Office Impressions, 20 lbs) with an 80 mesh flat bed screen purchased from Sefar. The thickness of the dried CuO print was measured to be 60 μm. The resulting prints were dried overnight under ambient conditions before being processed on the PulseForge 3300-X2 photonic curing system equipped with XP-492 lamps; the pulse structure depicted in Figure 1 was used. All processing was performed under ambient conditions at a conveyor speed of 30 ft/min. After processing, the cured circuits were covered with a thin layer of fixative spray to prevent re-oxidation of the Cu circuit. The radiant exposure of each pulse was measured using a bolometer. The thickness of the dried prints and paper substrates were measured with a Mahr Extramess 2000 digital comparator. The total resistance of the circuit after photonic curing was measured with a Fluke 175 True RMS Multimeter. Scanning electron microscopy (SEM) images were collected with a Zeiss microscope equipped with an InLens detector operating at a 5 kV accelerating voltage. X-ray diffraction (XRD) was performed on a Rigaku R-Axis SPIDER diffractometer equipped with a Cu Kα radiation (λ = 1.54059 Å) source and an image plate area detector. The current capacity testing was performed with a BK Precision model 9123 programmable DC power supply. In order to standardize the current capacity testing, the samples were suspended in air to minimize heat conductive heat transfer and normalize the heat loss due to convective heat transfer.

Results and Discussion

Metalon ICI-021 is screen printed into uniform and defect-free circuits. The ICI-021 contains irregularly shaped CuO flakes of varying sizes and a thermally-activated reducing agent package. Figure 2A shows how the polydispersed flakes form a densely packed print. Figure 2B shows that on a larger scale, the prints are featureless and uniform. As shown in Figure 2C, the photonic curing process significantly alters the morphology of the printed circuit. After photonic processing, the Cu generated from the reduction of CuO sinters into a denser film on a microscopic scale. However, on a larger scale, Figure 2D, the film exhibits features resulting from volume loss due to gas generation during the reduction process as well as loss of free volume due to sintering. The cured circuit looks non-uniform but it is reduced to conductive Cu throughout the film. A cross-sectional microscopy image of the processed circuit, Figure 3, reveals that although only the top surface is fully sintered, the print is reduced to Cu deep below the surface. Previous work established that CuO on paper substrates could be processed at thicknesses of up to ~ 50 µm. Although thicker prints could be made, the energy required to react deeper into the circuit damaged the paper substrate.[10]

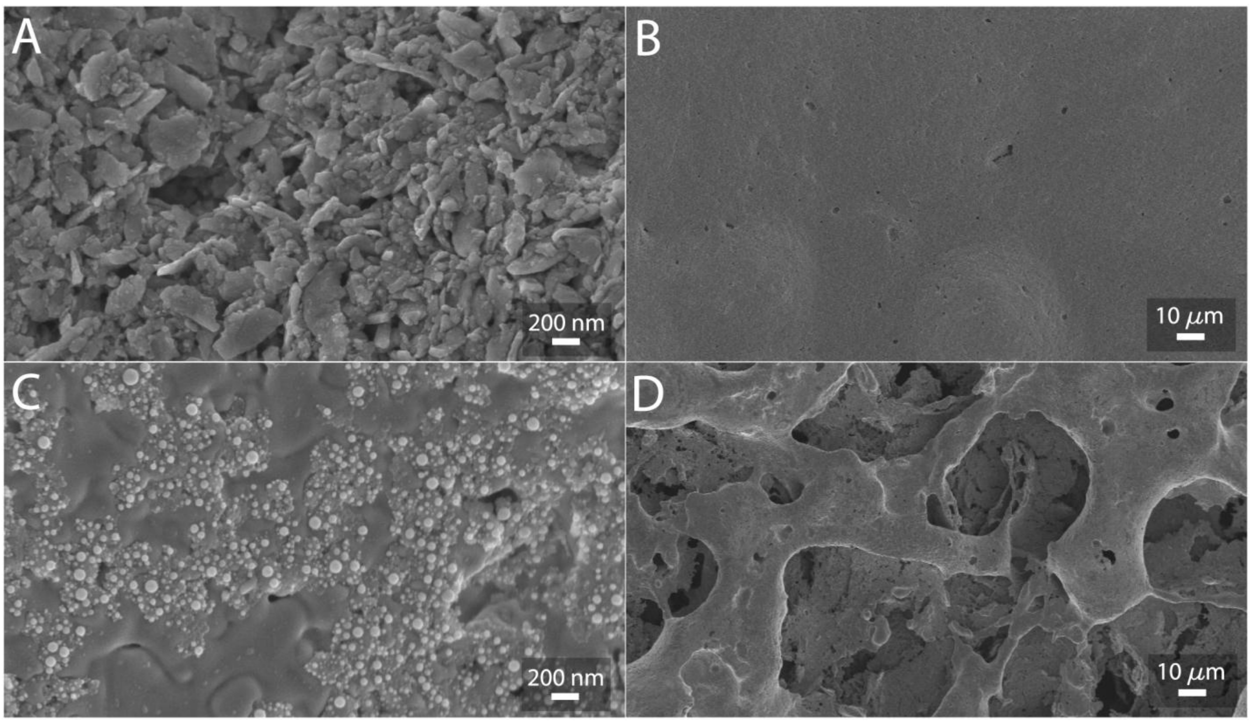

Figure 2: SEM images of (A–B) as deposited and (C–D) photonically cured ICI-021 prints at varying magnifications.

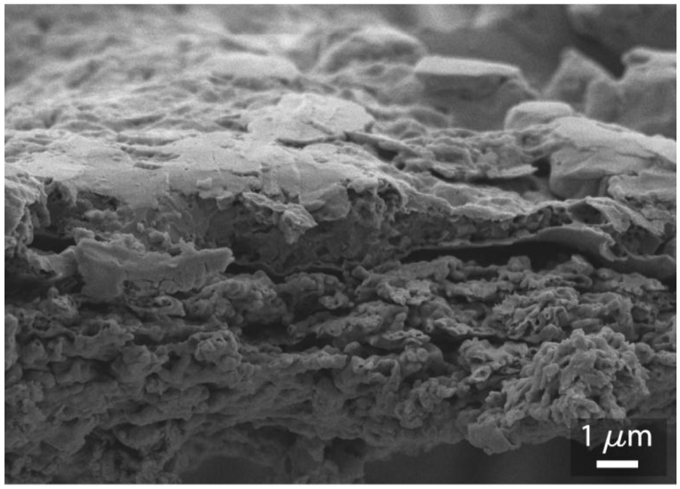

Figure 3: Cross sectional SEM image of photonically cured ICI-021 prints on paper.

Analysis of XRD spectra of the printed ICI-021 circuits at different stages of processing reveals how the photonic curing process impacts the compositional and crystallographic makeup of the print. The spectrum in Figure 4(i) shows that as-deposited prints are composed completely of monoclinic CuO. The reducers present in the ink are not crystalline and are not represented in the XRD data. The threshold of conversion to face-centered cubic (FCC) Cu is reached at around a radiant exposure of 5.6 J/cm^2, Figure 4(ii). At this stage, only a small amount of Cu was present in the film and the circuit was not conductive. Increasing the radiant exposure to 6.8 J/cm^2 produced conductive circuits (45 mΩ/sq) and a dominant presence of FCC Cu, Figure 4(iii). A further increase of radiant exposure to 9.8 J/cm^2 results in more conductive circuits (20 mΩ/sq) and a film with a majority FCC Cu, Figure 4(iv). For fully cured circuits, a small fraction of body-centered cubic (BCC) Cu_2O was present, but no residual monoclinic CuO was detected. When the radiant exposure was increased even more (up to 11.5 J/cm^2) overcuring of the print occurred and the circuit was broken (no longer conductive). This change is accompanied by a darkening of the circuit and a re-oxidation of the reduced Cu. The spectrum in Figure 4v shows that the re-oxidized Cu was in the form of BCC Cu_2O.

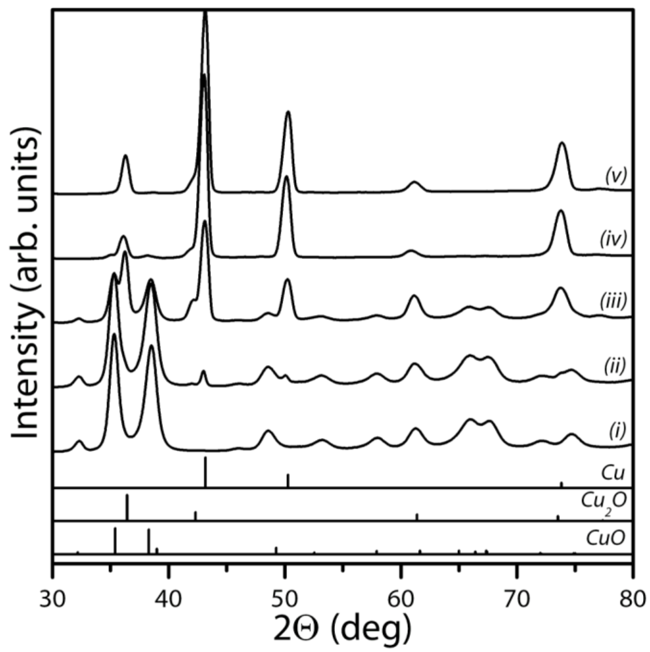

Figure 4: XRD spectra of ICI-021 CuO reduction ink (i) as printed, (ii) at the onset of reduction, (iii) undercured, (iv) fully cured, and (v) overcured. Reference diffraction spectrums of Cu (PDF#01-071-4611), Cu2O (PDF#01-071-3645), and CuO (PDF#01-089-2531) are plotted for comparison.

For many applications, the current carrying capacity of thin inkjet-printed circuits is insufficient. For this reason, screen printing and curing thicker depositions is important to build higher power circuits. Figure 5 plots how the current carrying capacity of the circuit changes with changes to the curing depth in the print. The depth of cure and the resistance of the circuits depended on the radiant exposure used for the processing. The dashed line in Figure 5 is a fit to the current carrying capacity, e.g. failure point, of each circuit. As is typical with the actioning of a circuit, failure initiates at local defects in either the trace or the substrate. The typical I^2R power dissipated in the circuit at failure was 2-3 W independent of the sheet resistance of the trace. This suggests the failure was related to the temperature at which the circuit attained from joule heating. Since the area of the trace was 2.8 cm^2, this corresponds to ~1 W/cm^2 at failure. Using SimPulse™ thermal stack simulation software (resident on every PulseForge tool), we balanced the joule heating of the circuit with the natural convection losses on both sides of the stack to calculate that the temperature reached at failure was ~200 °C. This is not unexpected as it is just below the thermal decomposition temperature of the substrate.

When approaching the current limit, the circuit heats up at a single point and oxidizes, or leads to burning of the paper substrate. Overall, the current capacity of the circuit is based on the resistance of the tested circuit and the frequency of defects in the circuit. The circuit is capable of carrying higher currents when the circuit resistance is lower and the defect frequency is less. The circuits shown in Figure 5 were relatively defect free and thus each failed at a similar power level. We were able to demonstrate current carrying capacity of up to 1.4 A in a 14 mΩ/sq print. Circuit design and cure depth play important roles in determining the current capacity of the circuit. An objective of the current development work is to use the higher current capacity of the printed Cu prints to build power delivery circuits. These results allow us to predict the current carrying capacity of other prints as the sheet resistance of our circuits continues to be reduced.

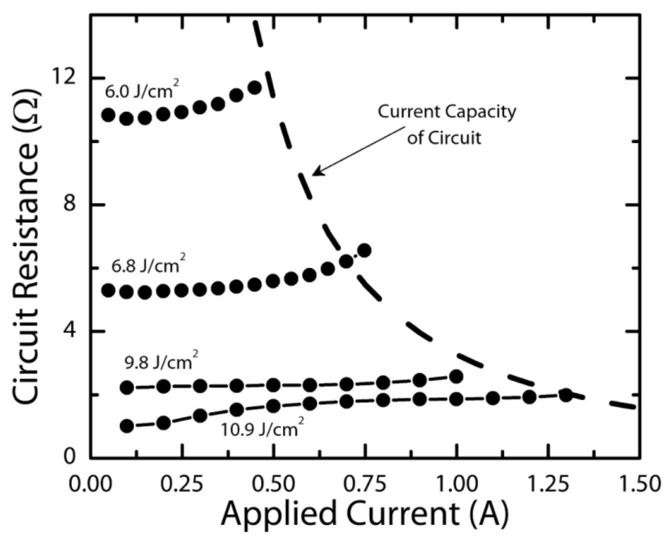

Figure 5: The variation of the resistance of the printed circuit with applied current for circuits cured at different radiant exposures (in J/cm^2). The circuit is irreversibly damaged at high current and the dashed line indicates the experimental determined current capacity of the circuit.

Summary

The printed electronics industry aims to produce high volume and inexpensive electronic devices by utilizing existing printing infrastructure and adding new functionality. The PulseForge tools and Metalon inks provide a versatile platform for accomplishing the goals of the printed electronics industry. The PulseForge tools have many unique features and can be incorporated into existing roll-to-roll processing equipment. The Metalon inks provide new functionality and new material systems that can be printed using existing printing equipment. The combination of the two provides a route to printing highly conductive circuits on low cost and flexible substrates.

We have demonstrated the printing and curing of thick circuits on paper substrates. By using thermal simulation (with the SimPulse™ thermal stack simulation, developed in-house and discussed in previous publications[7,10]) and pulse shaping, we identified improved processing parameters for achieving more thorough curing of thick-film printed circuits. The deeper cure results in higher conductance circuits with very high current capacities. Sheet resistances as low as 11 mΩ/sq were obtained. We have also demonstrated that circuits with a slightly higher sheet resistance, 14 mΩ/sq, could carry up to 1.4 A of current without degradation.

References

1. Schroder, K.A. (2011), "Photonic Curing Explanation and Application to Printing Copper Traces on Low Temperature Substrates", Technical Proceedings of the 2011 NSTI Nanotechnology Conference and Trade Show, Vol. 2, pp. 220–223.
2. Schroder, K.A., Rawson, I.M., Pope, D.S., and Farnsworth, S. (2011), "Printed Electronics: Photonic Curing Tools and Copper Inks", IMAPS Fall 2011, San Jose, CA.
3. Kang, J.S., Ryu, J., Kim, H.S., and Hahn, H.T. (2011), "Sintering of Inkjet-Printed Silver Nanoparticles at Room Temperature Using Intense Pulsed Light", J. Electronic Materials, Vol. 40, No. 11, pp. 2268–2277.
4. Langston, M.C., Dasgupta, N.P., Jung, H.J., Logar, M., Huang, Y., Sinclair, R., and Prinz, F.B. (2012), "In Situ Cycle-by-Cycle Flash Annealing of Atomic Layer Deposited Materials", J. Phys. Chem. C, Vol. 116, pp. 24177–24183.
5. Brombacher, C., Schubert, C., Daniel, M., Liebig, A., Beddies, G., Schumann, T., Skorupa, W., Donges, J., Haberlein, S., and Albrecht, M. (2012), "Chemical Ordering of FePt Films Using Millisecond Flash-Lamp Annealing", J Appl. Phys., Vol. 111, pp. 023902.
6. West, J., Carter, M., Smith, S., and Sears, J. (2012), "Photonic Sintering of Silver Nanoparticles: Comparison of Experiment and Theory", Sintering - Methods and Products, 173–188, InTech Publishing.
7. Farnsworth, S., Schroder, K., Wenz, B., and Rawson, I. (2012), "Broad Implications Arising from Photonic Curing Process for Printed Electronics and Displays".
8. Kamyshny, A., Steinke, J., and Magdassi, S. (2011), "Metal-based Inkjet Inks for Printed

Electronics", Open Applied Physics Journal, Vol. 4, pp. 19–36.

9. Ryu, J., Kim, H.S., and Hahn, H.T. (2011), "Reactive Sintering of Copper Nanoparticles Using Intense Pulsed Light for Printed Electronics", J. Electronic Materials, Vol. 40, No. 1, pp. 42–50.
10. Akhavan, V., Schroder, K., Pope, D., Rawson, I., Edd, A., and Farnsworth, S. (2013), "Reacting Thick-Film Copper Conductive Inks with Photonic Curing", ICEP 2013, Osaka, Japan.