Reacting Thick-Film Copper Conductive Inks with Photonic Curing

V. Akhavan, Ph.D.; K. Schroder, Ph.D.; D. Pope, Ph.D.; I. Rawson; A. Edd; S. Farnsworth*
NovaCentrix®
200-B Parker Dr, Suite 580, Austin, TX 78758, Phone: +1-512-491-9500
*Corresponding Author: stan.farnsworth@novacentrix.com

Abstract

Photonic curing is an effective process for heating inks and functional films to very high temperatures, in excess of 1000°C, on temperature sensitive substrates such as paper, polymer, or fabric. The use of this thermal processing method has been explored previously in the literature for sintering, annealing, and reacting materials such as metal-based electrically conductive inks. The authors now apply this technique to ink depositions greater than 10 µm thick and show that pulse conditions as well as pulse architecture play a key role in producing good results. Cu circuits with sheet resistance as low as 11 mΩ/sq were achieved on paper by screen printing and photonic curing thick depositions of CuO reduction ink.

Introduction

Photonic curing is high-temperature thermal processing of thin films using pulsed light from a flashlamp. Photonic curing has the ability to cure high temperature materials on temperature sensitive substrates. This, coupled with the speed of the process, makes photonic curing compatible with roll-to-roll manufacturing and has additionally resulted in the synthesis of new material systems. Recent reports have demonstrated that the photonic curing process can be applied to a wide range of materials and applications.(1-4)

The standard pulsed light intensity profile structure for processing inkjet inks is approximated as a square wave, producing a single peak temperature in the target materials. This type of heating profile works well for very thin films.(4) For a variety of applications, however, thicker films are desired.

The square pulse structure is generally not suitable for processing thicker films of reactive materials such as the Metalon® ICI copper oxide reduction ink.(5-6) A square pulse can cause overheating in the upper parts of the thicker prints, resulting in undesired reactions while leaving unreacted layers in the deeper sections of the film. The authors have determined that a composite (segmented) pulse structure is more effective at processing depositions greater than 10 µm thick.

New designs of photonic curing equipment have led to the development of the state-of-the-art PulseForge® tools. The PulseForge tools are water cooled flash lamps that turn on and off the radiation source over very short time scales (< 50 µs). This capability allows modulation of pulses faster than the thermal equilibration time of the substrate. As such, a square pulse can be divided into discrete sub-pulses to change the heating rate and processing time of the film. Figure 1 illustrates the difference between a square pulse and a composite pulse. The “ON” times of both pulses are equivalent (4100 µs), but the composite pulse is composed of multiple shorter pulses separated from each other to provide a different heating and cooling profile.

The composite pulse modulates faster than the thermal equilibration of the materials stack. As such, the resulting thermal gradient is much different than a square pulse. By judiciously tailoring the pulse conditions, it is possible to construct a pseudo ramp-and-soak processing step. This type of processing is well suited for printed electronics applications where precise tailoring of the temperature time profile has a profound effect on performance.

In this report, Metalon CuO reduction ink (ICI-021) is screen printed onto a paper substrate and reduced to a metallic and conductive Cu pattern. The reduction process on the temperature sensitive paper substrate is a transient effect enabled by photonic curing. We demonstrate that more conductive circuits can be fabricated through the use of composite pulses.

Objective

Currently, printed electronics designs focus on inkjet printed Ag inks. High raw material costs of Ag inks as well as print thickness limitations of inkjet printing have thus far prevented wide-spread adoption of printed electronics. In this report, we discuss screen printing and photonic curing of thick depositions of inexpensive CuO inks. The objective is to review the optimized route to photonically cure thicker depositions of these inexpensive reactive materials

The response of the CuO deposition to photonic curing is complex. Multiple changes in the film impact the final print conductivity. A few of the important variables are listed here.

- Reduction reaction
- Re-oxidation reaction
- Thermal conductivity of the substrate
- Blow off of the printed circuit
- Displacement due to thermal expansion

Because of the strong correlation between print conductivity and processing conditions, the final conductivity of the circuit is a good indicator of processing conditions. For example, converting the CuO to Cu deeper into the print thickness results in a more conductive circuit.

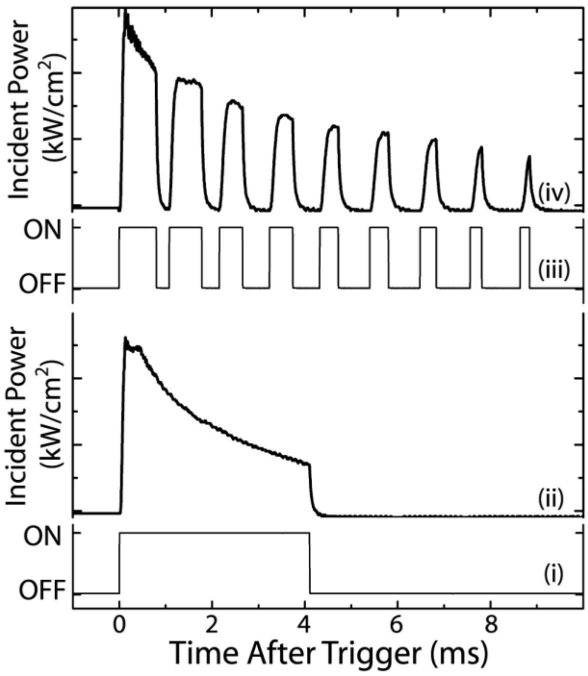

Figure 1: Illustration of (i and iii) current through the switch and (ii and iv) the resulting output from the flash lamp for the square pulse and the composite pulse used for this work.

Methods

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) or card stock paper (Wausau Paper, Exact Index, 110 lbs) with varying mesh size flat bed screens (325, 230, 165 or 80 mesh). 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. All processing was performed under ambient conditions at conveyer speed of 30 ft/min. The radiant exposure of each pulse was measured using a bolometer. Thickness of the dried prints and paper substrates were measured using a Mahr Extramess 2000 digital comparator. The total resistance of the circuit after photonic curing was measured using a Fluke 175 True RMS Multimeter.

Applications and Results

The effect of both the square wave and segmented pulse profile were simulated using the tool integrated SimPulse^{TM} thermal stack simulation. Inputs to the simulation are the thicknesses and thermophysical properties of the substrate and the film as well as the inputs to the waveform settings on the PulseForge tool. Figure 2 depicts the resulting thermal profile output in the sample with the pulse structures depicted in Figure 1. To effectively process the CuO reduction inks, which contain CuO and a reducer, a certain threshold temperature must be achieved. If the CuO print remains below this temperature (in the cold zone), the reducers are not activated and the reduction reaction does not occur. On the other hand, the print cannot be overheated as the resulting temperature deteriorates the print through the re-oxidation of the Cu and effectively convert the film back into an insulator. The exact threshold temperatures are not known but we have estimated the values through experimental observations.

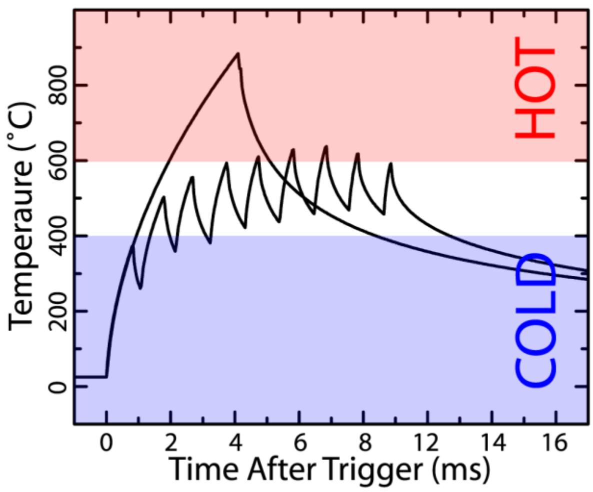

Figure 2: Simulated temperature of the surface of the materials stack due to the single square wave and segmented pulse conditions of Figure 1.

The complexity of the changes in the print as a result of photonic curing limits us to a narrow temperature range where the desired reactions are favored. Through design of a composite pulse structure, we can maximize the time that the print remains within the proper temperature range. Figure 2 illustrates the simulated temperature profile output from both sets of pulse profiles. Specifically, a square pulse profile results in overheating of the printed circuit followed by rapid cooling to a temperature below the reaction threshold. In contrast, the composite pulse results in print temperatures remaining in the optimized reaction zone for a longer period of time without a spike into the undesirable "hot" zone. An optimum pulse condition enhances the desired reactions through thermal control of the system.

Figure 3 shows prints photonically cured with varying amounts of radiant energy. The un-processed print shown in Figure 3A is black and non-conducting. Figure 3B shows an optimally cured print which exhibits very little variation in color and conductivity along its length. The uniformity of both the light source and the print results in the homogenous reduction of CuO to Cu. If the radiant exposure to the film is increased, the print temperature remains elevated long enough for the copper to begin to re-oxidize. This undesirable re-oxidation can be seen in Figure 3C where the color of the print has darkened from bright orange to a dull brown. The print also exhibits an increase in resistance. If the radiant exposure is increased further, the temperature of the print increases to the point that rapid vaporization and decomposition of the ink constituents causes the print to "blow off" of the paper resulting in a non-conductive print. Figure 3D shows this blow off effect. Interestingly, the highest conductivities are achieved at exposure levels just below those which cause physical damage to the print.

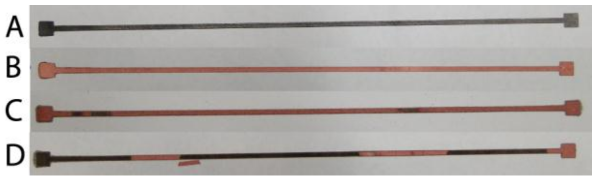

Figure 3: Photographs of (A) as-deposited, (B) optimally cured, (C) reoxidized and (D) flaking circuits.

Figure 4 illustrates the depth to which the reduction reaction has occurred based on microscopy measurements of the print. The color change from black CuO to orange Cu is easy to visualize. Figure 4A shows the unprocessed print which is black throughout the print thickness. A mild pulse condition leads to surface reduction of the print (Figure 4B) and a relatively high sheet resistance (60 mΩ/sq). Increased pulse energy promotes conversion of CuO to Cu deeper into the print (Figure 4C) resulting in a lower sheet resistance (15 mΩ/sq). Conversion of CuO to Cu through the depth of the print is possible using either square or composite pulse designs; however, pulse shaping reduces undesired side reactions thereby allowing higher conductivity values to be achieved.

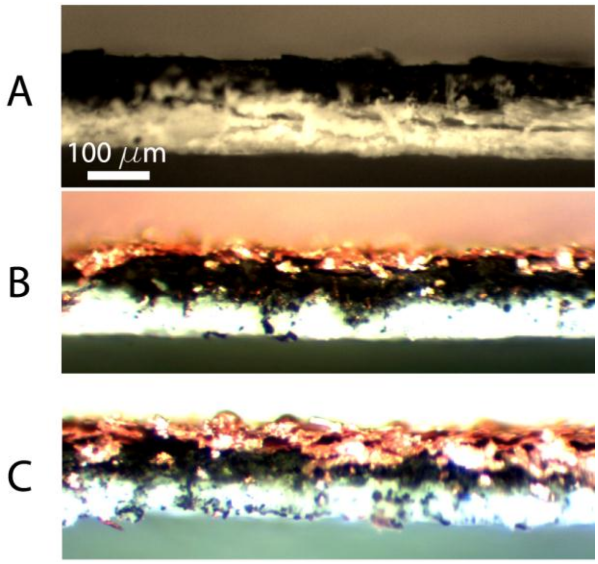

Figure 4: Microscopy images of (A) as-deposited and (B–C) photonically cured CuO prints on copy paper.

Figure 5A plots sheet resistance for 165 mesh prints on copy paper (30 μm thick prints) as a function of radiant exposure. The open circles show the results of processing with a square pulse and the filled circles show the results of processing with composite pulses. Regardless of the pulse shape, the lowest sheet resistance values are achieved at radiant exposure of approximately 8 J/cm^2. The prints begin to degrade at radiant exposure above 9 J/cm^2. By comparing the minimum sheet resistance values, we see that the composite pulse produces a sheet resistance approximately 20% lower than a simple square pulse. The improved results are due to the control of temperature in the print. Through pulse shaping, it is possible to minimize hotspots in the film and reduce undesired reactions.

The temperature profile within a material stack during photonic curing is not only a function of the input curing waveform. Changes in thicknesses of the printed trace as well as the thickness of the substrate will impact the heating rate and temperature profile. Two different paper thicknesses were studied in this work. The card stock was approximately 200 μm thick, and the copy paper was approximately 85 µm thick. ICI-021 was printed on both papers using an 80 mesh screen, resulting in 80 µm thick prints. Figure 5B plots the cured print sheet resistance achieved on each paper substrate at various pulse energies. The sheet resistances of the prints on the thinner copy paper are slightly lower than the prints on the thicker card stock paper. The differences are due to the lower thermal mass per area of the copy paper which leads to longer heat retention and deeper processing of the print for a given amount of radiant exposure.

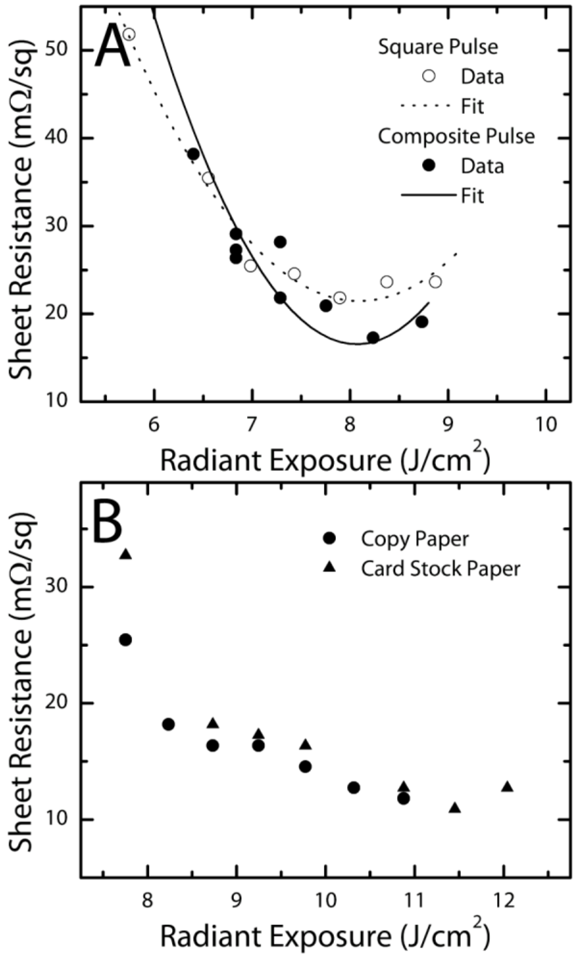

Figure 5: (A) Sheet resistance of traces cured with square or composite pulse structure. (B) Sheet resistance of traces cured on two different thickness paper substrates.

Figure 6 shows how the minimum sheet resistance achieved in as-processed prints changes with pulse shape, substrate type, and print thickness. As expected, the thicker prints exhibit higher conductivity (hence lower sheet resistance). The lowest sheet resistance achieved with this work was 11 mΩ/sq. We note that the composite pulse structure produces a lower sheet resistance regardless of the print thickness or substrate thickness. In addition, these data provide further evidence that the prints on the thinner copy paper exhibit a lower sheet resistance than those on the thicker card stock. As expected, the sheet resistance values decrease with increasing print thickness. However, the sheet resistance values remain relatively unchanged for print thicknesses greater than about 50 µm indicating a limit to the curing depth. Although the PulseForge tools are capable of producing higher energy pulses, the paper substrate begins to degrade at radiant exposure energies beyond about 10 J/cm^2, which effectively limits the maximum curing depth. Fortunately, the complexity of the CuO reduction reaction leaves room for further improvement in pulse shaping and is an active area of research at Novacentrix®.

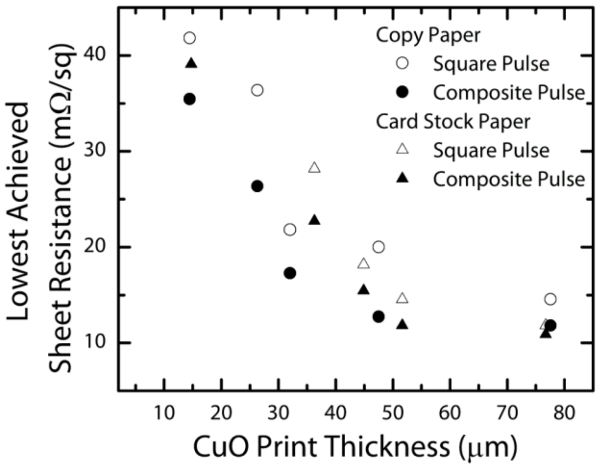

Figure 6: Lowest achieve sheet resistance at different print thicknesses.

Discussion and Summary

The goals of the printed electronics industry remain to produce both high volume and inexpensive electronic devices by utilizing the existing printing infrastructure as well as adding new functionality. To this end, the PulseForge tools provide a curing platform compatible with high speed printing techniques. The PulseForge tools can be incorporated into existing roll-to-roll processing equipment to provide an economic as well as a performance advantage to printed electronics manufacturing processes. This work demonstrated how the fast turn on and turn off rates of the PulseForge tools can be utilized to photonically cure thick-printed depositions using inexpensive materials to achieve the higher conductivities needed for the printed electronics infrastructure.

By using thermal simulation and pulse shaping, a complex curing profile can be designed to process a specific material accounting for complex reaction mechanisms. In this report, we demonstrated this process with the photonic curing of thick prints of Metalon ICI-021 CuO reduction ink on paper substrates. Here, a composite pulse structure was designed to provide a longer ramp-and-soak processing step than possible with a simple square pulse. The new pulse design maintains the printed material within a defined temperature range to achieve sheet resistances as low as 11 mΩ/sq on ordinary copy paper.

Related Works

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[5] 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.

[6] K. A. Schroder, Rawson, I.M., Pope, D.S., and Farnsworth, S. (2011), “Printed Electronics: Photonic Curing Tools and Copper Inks”, IMAPS Fall 2011, San Jose, CA.