**Printed Electronics: Photonic Curing and Enabled Materials**

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**Extended Abstract**

**Introduction**

Photonic curing is a transient thin-film thermal processing technique using flashlamps. It was developed by NovaCentrix® and incorporated into the PulseForge® toolset to address the need of the printed electronics industry to process high temperature materials on low temperature substrates such as paper and plastic on a moving web. Applications include photovoltaics, displays, solid state lighting, thin film batteries, RFID tags, and printed circuits. The ability to substitute inexpensive and flexible substrates for expensive, rigid substrates while achieving similar performance can dramatically reduce the cost of the final product and enable new products. In this paper, we discuss the technology and mechanisms of the process and illustrate a case study of forming copper traces on plastic and paper in a roll-to-roll environment. Here, a low cost copper oxide ink is printed on plastic or paper and chemically reacted using pulsed light from the PulseForge tool to form highly conductive copper traces. This process is performed in an ambient atmosphere.

Figure 1 illustrates the main effect we exploited. A high power, short pulse of light from a flashlamp is used to heat a thin film of material, such as printed silver or copper nanoparticles or flakes, to a high temperature for a brief amount of time. This can be done on a low-temperature substrate, such as polyethylene terephthalate (PET). Normally, PET has a maximum working temperature of 150 °C. With this technology, a thin film can be processed beyond 1000 °C on the surface of a PET substrate without damaging it, provided it is heated up and cooled down very quickly. This is an adequate temperature to sinter many materials including silver and copper. The pulse of light is so fast that the back side of the substrate is not heated appreciably during the pulse. After the pulse is over, the thermal mass of the substrate rapidly cools the film via conduction. The pulse is usually less than a millisecond in duration, and the time spent at elevated temperature is only a few milliseconds. Although the substrate at the interface with the thin film reaches a temperature far beyond its maximum working temperature, there is not enough time for its mechanical properties to be significantly changed. This effect is highly desirable as the thin film has now been processed at a temperature which would severely damage the substrate if processed with an ordinary oven. It often allows the replacement of high-temperature substrates with lower-temperature (e.g. cheaper) alternatives. Since most thermal processes are Arrhenius in nature, i.e., the curing rate is related to the exponential of the temperature, this short process can, in many cases, replace minutes of processing in a 150 °C oven! This further means that if the light is pulsed rapidly and synchronized to a moving web, it can replace a large festooning oven in a space of only a few feet. In addition to curing materials quickly, higher temperature materials such as semiconductors or ceramics that cannot ordinarily be cured on a low-temperature substrate can now be cured using this technology.

One of the more remarkable aspects of this technology is that materials can be cured with the economics and uniformity of oven curing but also with the control of laser processing. Photonic curing is completely maskless. Printed thin-film traces are heated while the surrounding substrate is not. This can happen because most inexpensive substrate materials, such as PET, PE, PEN, PC, PI, or even paper, do not readily absorb light. More specifically, the absorption depth for most of the emission from our system
is much larger for those materials as compared to many of the materials suitable for functional inks and thin films. Thus, the substrate does not get as hot as the thin film does. This effect allows one to cure a printed thin film with pulsed radiation on a low-temperature substrate without the need for registration. Of course, the substrate underneath the film does get much hotter than its maximum working temperature, but it does not become damaged. We address that below.

**Case Study: Converting CuO into Cu**

Using PulseForge tools, electronic inks originally designed to be cured on expensive, high temperature substrates by conventional processes such as convection ovens, IR curing, or UV curing, can instead be used successfully on low temperature substrates. Usually, the PulseForge-processed inks meet or even exceed results of conventional processing when cured on plastic or paper. This has allowed rapid deployment of the PulseForge tools since an immediate benefit has been realized. However, when inks are designed specifically for use with PulseForge tools, the performance is much greater. We have been able to create new types of films. One such film is copper.

Copper has long been the desired material as a conductor for printed electronics. Currently, copper is over 100 times cheaper than silver yet has over 90% of silver’s electrical conductivity. Still, silver remains the dominant conductor in printed electronics. The reason a precious metal is still used over copper is almost exclusively related to the propensity of copper to oxidize. Printing copper means that small particles, usually nanoparticles, of copper need to be synthesized, dispersed and formulated into an ink, printed, and sintered to form a conductor. Since copper oxide does not appreciably conduct electricity, protection from oxidation is needed at all stages. Since the sintering stage is high in temperature, it is the most critical. If there is any oxygen present when attempting to sinter using traditional thermal processes, the particles will oxidize before they sinter. This problem forces the use of ovens filled with inert gas, or for even better performance, with explosive hydrogen gas. Before photonic curing, the sintering procedure was generally a slow batch process.

NovaCentrix addressed the problem of copper oxidation with photonic curing and was awarded a US patent for the effort. The photonic curing process is so fast that the copper particles sinter before they appreciably oxidize, so unlike other sintering processes, it can be done in ambient air. Furthermore, the speed of the process and the elimination of the requirement for a special atmosphere enabled the sintering of thin film copper almost instantly in a reel-to-reel environment. However, there is one problem. Nanocopper powder is often more expensive than nanosilver powder. This additional cost of keeping the particles and dispersions oxygen free negated many of the benefits of using photonic curing to overcome the oxidation during the sintering process. We came to the conclusion that inexpensive particles and dispersions are key to enabling an inexpensive process.

**A paradigm shift**

We decided that instead of fighting the oxidation of copper, we would begin with pure copper oxide, formulate it with a reducer, and modulate the redox reaction with the beam from the PulseForge tool to form pure copper. This is a step beyond viewing photonic curing as just a drying or sintering process. In this case we are modulating a high temperature reaction on a low temperature substrate.

A reducible copper oxide ink approach has several advantages over a pure copper ink. First, copper oxide is inherently cheap. Nanoparticles of copper oxide are more than order of magnitude cheaper than nanosilver or stabilized nanocopper. Copper oxide particles have more surface charge than copper particles, so they are easier to disperse. Copper oxide is also very thermodynamically stable, meaning we don’t have to worry about it oxidizing! Similar to the copper sintering, the process happens so quickly that copper oxidation from the atmosphere during the reduction reaction is avoided, so a pure copper film can be formed in open air. Like the copper sintering process, the ink cannot be cured with an oven.
Curing with PulseForge equipment is required to convert the copper oxide ink.

Figure 2. shows a screen print version of the copper oxide reduction ink on ordinary paper before and after processing with a PulseForge tool. The sheet resistance before curing is of order 1 GΩ/sq, and after curing the sheet resistance is approximately 60 mΩ/sq. That is, the conductivity is increased by approximately 8 orders of magnitude in about 1 millisecond. As expected, the trace turns from the black color of copper oxide to the familiar shiny hue of pure copper. In addition to the screen-print formulation of the copper oxide reduction ink, we have also developed an inkjet version as well as inks for flexographic and gravure processes. Figure 3 shows several RFID antennae printed on coated PET. The bulk resistivity is about 3X bulk copper. Both of these reduction inks are water-based and low VOC. Figure 4 shows SEM cross sections of a print before and after processing. A densification and reduction in surface area of the trace is easily seen.

The current PulseForge system used to do this processing is shown in Figure 5. It uses Pulse Width Modulation, so that any pulse length, shape, and profile can be created. This is a first for a flashlamp-based system, and we found the capability necessary for tuning the temperature profile within a thin film stack for optimal processing. We have also created a computational thermal stack simulator, called Simpulse™, and integrated it into the PulseForge tools to predict the thermal profile of a thin film stack as a function of the 10 continuously adjustable process variables of the Pulse Forge tool. This predictive simulation makes it possible to model the sintering or annealing of many types of materials including metals, semiconductors, and even ceramics – all on low-temperature substrates.
Figure 1. Thermal simulation of the photonic curing process (300 μs, 1 J/cm²) for a 1 micron thick silver film on 150 micron thick PET. Temperatures beyond 1000 °C can be achieved on PET without damage.
Figure 2. Image of screen-printed copper oxide reduction ink before and after conversion to copper in open air on Paper. Note the pronounced color change after processing.

Figure 3. Inkjet version of the copper oxide reduction ink on coated PET after conversion to copper. Shown are RFID antennae.
Figure 4. SEM cross-sections of copper oxide ink trace before and after reduction to copper. Note the decrease in surface area and densification of the film.

Figure 5. PulseForge® 3300 photonic curing system.