Photonic Curing as Means for Converting Copper Oxide to Copper on Low Temperature Substrates, with Application in RFID

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Abstract

Photonic curing has previously been described by the authors as an effective means for thermal processing of high-temperature films on low-temperature substrates using flashlamps. The authors review this technique as well as implications in the development of novel inks using this technique to convert copper-oxide-based inks to copper in an ambient atmosphere on low-temperature substrates such as paper and plastic. Specifically, the curing equipment and ink platform, both commercially available, are applied to the printing of RFID antennae. Preliminary results are presented of the performance and cost of this application. Portions of this paper have previously been presented by the authors.

Keywords: printed electronics, screen inks, inkjet inks, rfid, conductive, silver, reduction, copper, photonic curing

Introduction

Light and radiation-based materials processing have long been used for industrial and graphics applications. The authors have previously presented the photonic curing technique as an emerging method also using light for thermal and UV-based processing of materials, but with a novel caveat. The energy delivery associated with photonic curing is in micro-second to millisecond time durations, and is used to induce a non-equilibrium response in the target materials. This processing method is well suited for application to printed electronics such as types of photovoltaics, batteries, flexible circuits, displays, and RFID. Specifically, this processing method resolves conflict of functional material processing temperatures with the thermal processing limits of polymers and paper, both substrates of interest in the printed and flexible electronics community. Printed electronics can be described as adapting the use of long-standing traditional printing methods, such as screen, inkjet, flexo, gravure, and spray deposition, to produce functional electronic devices. However, in order for the promise of printed electronics to be fulfilled, many advances are needed. These new applications often require the final devices to be flexible, or have cost/performance requirements which cannot be met using traditional manufacturing technologies or methods. This need has driven development of new technologies that are now leaving the R&D laboratories and being commercially deployed.

Photonic Curing

Photonic curing is a key technology developed to resolve the fundamental thermal processing challenge common to printed electronics, namely processing high-temperature functional materials, such as conductors, semiconductors, and dielectrics on low-cost flexible substrates such as polymers and paper. The photonic curing process uses pulsed light from a flashlamp to thermally process a thin film. The thin film, printed on a low temperature substrate, is heated by a brief but very intense pulse of light from a flashlamp. If the pulse of light is short enough, the thin film can be heated to a temperature far beyond the normal maximum working temperature of the substrate without damaging the substrate. This technique has been embodied in the PulseForge® tools produced by NovaCentrix®. .Figure 1 below depicts a typical PulseForge tool, including the primary module components (left- right) of:

- Heat exchanger
- Power rack
- Lamp Assembly (top)

- Material conveyor (bottom)
- Control module with touch-screen interface.

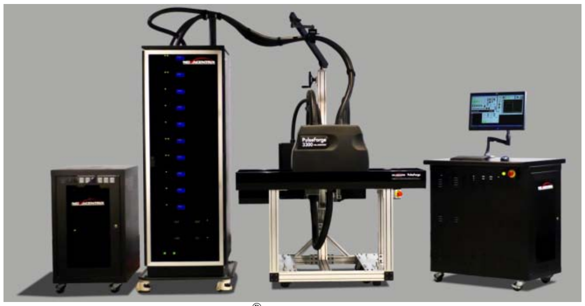

Figure 1. PulseForge® 3300 photonic curing system

Figure 2 illustrates the main thermal effect utilized by the process.

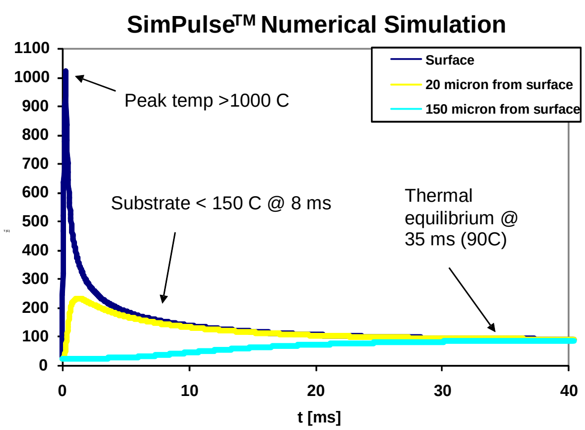

Figure 2. Thermal simulation of the photonic curing process (300 μs, 1 J/cm²) for a 1 micron thick silver film on 150 micron thick PET. Temperatures beyond 1000 °C can be achieved on PET without damage.

A high power, short pulse of light 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, we can process a thin film beyond 1000 °C on the surface of a PET substrate without damaging it, provided we heat the thin film up and cool it 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. Photonic curing 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.

The use of this method makes possible thermally processing films on plastic and paper that previously required expensive, high temperature substrates such as glass or ceramic. Typical processing times are about 1 millisecond, meaning that a photonic curing system can cure near-instantly. This quality makes it compatible with high-speed roll-to-roll processing. Initially, this process was used to sinter printed metal nanoparticle inks such as silver and copper to form electrical conductors. It is now being used to sinter higher temperature materials such as ceramics and semiconductors. In addition to sintering, photonic curing is being used to dry films as well as anneal and modulate chemical reactions to make new types of materials.

Enabled Material: Copper Oxide Conductive Inks

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. 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.

NovaCentrix addressed the problem of copper oxidation with photonic curing and was awarded a US patent as well as several commercial awards for the effort. Instead of fighting the oxidation of copper, the copper oxide inks are based on the use of copper oxide nanoparticles combined with a reducing agent. The particles are then converted to copper by modulating the redox reaction with the beam from the PulseForge tool.

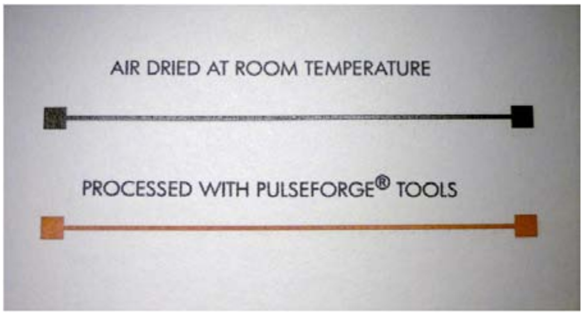

Figure 3: Image of screen-printed copper oxide reduction ink before and after conversion to copper in open air on Paper. Note the pronounced color change after processing.

Figure 3 shows a screen print version of the copper oxide reduction ink (Metalon® ICI-021) 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. These reduction inks are water-based and low VOC.

Example Application: RFID Antenna

The authors used the ICI-021 screen ink to produce the RFID antenna shown in Figure 3 below, on 110lb paper as the substrate.

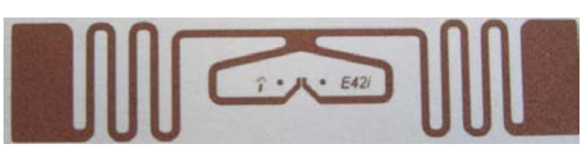

Figure 4. Screen-printed RFID antenna on paper after conversion to copper.

The tag is an Impinj® E42i and is produced under license. The tag is a printed area of 422 mm^2. The ink was deposited with a mesh 165 screen with emulsion thickness of 0.6 thousandths of an inch. This results in a measured ink thickness, dried, of approximately 10 microns. With these dimensions, and with a volume ink price of $75/kg, the ink cost per tag is determined to be approximately $0.003.
This tag was completed with the addition of a Monza 4 tag applied via anisotropic conductive adhesive. In our metal-framed lab we were able to achieve a read range of around 8-10 feet. There is much optimization to do at every step of the process, but these results are encouraging and, to our customers, merit moving forward with specific development efforts.

Summary

Photonic curing has been developed and advanced as a processing method successfully resolving a fundamental thermal processing challenge for printed electronics: Economical, high-speed, high-temperature processing of materials on low temperature substrates. The photonic curing tools have enabled in turn the development of novel ink formulations such as the Metalon ICI-021 copper oxide reduction inks. These inks then are being used to further reduce the costs of a number of printed electronics applications, with application in RFID presented above.

Customers and partners are rapidly moving to utilize this important new processing capability to establish or maintain market leadership with innovative and economical new products. Examples include the development and processing of novel photovoltaic materials, and production methods for batteries, displays, and sensors. As the adoption and use of the photonic curing tools continues to grow in the industry, the potential of printed electronics can truly be realized via new and innovative products.

Related Work

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