Evaluation of PulseForge Tool for Processing Metallic Conductive Inks on Low Temperature Substrates Part II: Screen Inks

S. Farnsworth; I. Rawson; K. A. Schroder, Ph.D.; D. Pope, Ph.D.
NovaCentrix®
200-B Parker Dr Suite 580, Austin, TX 78758
phone: (512) 491-9500, stan.farnsworth@novacentrix.com

Abstract

At this event in 2009, the authors discussed the need for advanced tooling and materials for printed electronics device development and manufacturing. We went on to describe and evaluate a novel toolset called PulseForge® which is based on photonic curing and capable of drying and sintering metallic-based inks on low-temperature substrates in milliseconds. Example inks manufactured by NovaCentrix used in the initial evaluation were silver and copper-based inkjet inks, with nanoparticles as the functional material. These inks were only 100's of nm thick when printed and dried. As part of on-going work, the authors are now presenting the same toolset applied to thicker screen print inks of silver and copper. A PulseForge 3100 in 12-inch width configuration is used to process improved silver screen ink on PET, and a new copper-based screen ink on copy paper. The tools produce equal or improved results over oven processing. Additionally, we demonstrate the PulseForge tools can process material at speeds consistent with volume manufacturing.

Keywords: printed electronics, screen inks, inkjet inks, rfid, battery, display, photovoltaic, conductive, silver, copper, photonic curing

Introduction

Part I of this paper[5], presented at this event in 2009 articulated the appeal of additive print-based manufacturing of electrical devices. Printing methods to deposit the functional electronic materials only where needed can allow the use of non-traditional material substrates such as polymers and even paper. These substrate materials are attractive because of their low-cost and because of their ability to flex and conform to non-rigid structures. The potential value of using these low-cost substrates integrated into devices such as displays, RFID antennas, batteries, and photovoltaics is projected to be hundreds of millions, or even billions, of dollars.

One of the biggest challenges in fabricating electrical devices on these low-cost substrates is that they are generally not capable of surviving the temperatures required to process functional inks. Researchers have worked to develop inks with lower processing temperatures. Progress has been made, and will continue to be made on the ink end. Still, researchers have generally engineered solutions for traditional oven processing. It would be desirable to have an advance in curing technology that didn't limit ink researchers to low temperatures. In short, there is a need to be able to process inks at higher temperatures while not damaging the low-temperature substrate. The PulseForge tools from NovaCentrix are designed for such a purpose.

Part I of this paper focused primarily on the use of conductive inkjet inks, characterized by the use of nanoparticles and in the thin nature of the depositions, generally below 500nm.

Part II presents follow-on information on the treatment of conductive screen print ink processing with the toolset, characterized by the use of flake morphologies and resulting in thicker (~5 micron) depositions.

Principle of Operation

PulseForge tools use intense pulsed light to heat thin films to high temperatures on low-temperature substrates without damage. This process is known as photonic curing. When the time of heating is long enough to uniformly heat the film but much shorter than the thermal equilibration time of the substrate, the film, even though it is in direct contact with the substrate, can be heated to a temperature much higher than the decomposition temperature of the substrate. Immediately after the heating, the thermal mass of the substrate "cools" the thin film via conduction. This rapid heating and subsequent cooling of the thin film prevents the substrate beneath it from being damaged.

Most curing processes follow an Arrhenius equation, that is, higher temperature processing results in much shorter processing time. Consequently, processing with PulseForge tools can be orders of magnitude shorter than traditional methods such as oven curing.

This transient, non-equilibrium thermal processing is accomplished with proprietary gas-discharge flash lamps which are cycled on and off in fractions of a millisecond to deliver the energy to the target material.

In the case of curing an ink on a low temperature substrate, the ink preferentially absorbs the light from a PulseForge tool over the substrate[1]. This allows broadcast curing without a mask.

Several parameters of both the ink and substrate such as thickness, thermal conductivity, heat capacity, optical absorptivity, melting point, boiling point, heat transfer coefficients at the surfaces as well as other parameters dictate the optimum power modulation of the PulseForge energy delivery system for curing.

Method Comparison

Ovens are the traditional processing method for curing functional inks on low temperature substrates. The principle advantages of oven processing include the capability of handling large areas, uniformity of temperature, and low cost. The primary disadvantage in using an oven for these applications is that the operating temperature is limited by the maximum working temperature of the substrate. Unlike drying graphics inks, curing functional inks generally requires additional thermal processing beyond just drying off the solvent. This temperature limitation means that oven processing generally takes minutes. In some cases, it cannot be done at all without going to a higher temperature (and more expensive substrate). In the case of roll-to-roll processing at industrial speeds, the size of the oven, even if it is festooned, becomes very large.

Lasers (solid state, excimer, CO_2) are commonly used for thin film processing. Lasers have the advantage of delivering high power for a short period of time enabling non-equilibrium thermal processing. They have two main limitations.

1) Cost: Laser processing as compared to oven processing is very expensive It is generally limited to only high value applications or small area processing.
2) Limited flexibility: Unlike an oven, laser curing systems are not generic or easily reconfigured without significant hardware changes. Attributes such as wavelength, beam size, power, and pulse length range are unique to a single system and are generally manufactured to a specific application.

In contrast, PulseForge tools combine the best of both ovens and lasers. Like an oven, processing is uniform. Since the system is modular, large areas can be handled. When processing at high rates, the cost of PulseForge tool processing is comparable to that of an oven. Like a laser, the beam from a PulseForge tool can be modulated in time enabling non-equilibrium thermal processing. Since the emitted spectrum from a PulseForge tool is broadband, it can be used for many types of applications. Finally, a PulseForge tool is very compact enabling it to be retrofitted into existing lines.

Equipment Description

Single exposures from fixed pulse length flash lamps have been referenced in the literature[3-5] with intriguing results. In the transition from a laboratory curiosity to an industrial piece of equipment we have developed a large area pulse light system capable of being modulated with a level of control similar to or even exceeding that of a laser. This allows us to adapt the power profile to that required of a specific film and substrate. This flexibility is needed due to the wide variety of inks and substrate combinations in commercial development.

NovaCentrix' first commercial tool designed for laboratory development, the PulseForge 1100, was released in 2007. While this tool has proven very versatile for processing many types of materials on many types of substrates, the manual, single pulse design of the tool makes it impractical for use in volume production. Consequently, in 2008 the PulseForge 3100 toolset (Figure 1) was released. It is designed for high-speed production of printed electronic devices.

Figure 1: PulseForge 3100 in 12" width configuration (from left):

- ***Lamp housing mounted over conveyor for stand-alone operation***
- ***Cooling system module***
- ***Power cabinet***
- ***Control module and operator station with touch-screen interface***

Key specifications for the PulseForge 3100 in 12" width configuration include:

Radiant exposure	0-5 J/cm^2
Pulse Duration	100 µs – 2 ms
Pulse Rate	0 – 300 Hz
Typical processing speed	10 m/min
Max speed (single-tool)	~100 m/min
Lamp lifetime	>>10^6 cycles
Processing cost	~$0.10/m^2

[Note: The PulseForge 3300 was released Nov 2009, with peak delivered radiant power as high as 50 kW/cm^2 and pulse lengths as short as 30 µs. In addition to processing metallic inks and UV materials, this tool can also process high temperature thin films such as semiconductors and ceramics.]

Test Materials for Part II

For this evaluation, three inks were selected.

Metalon® HPS-021 silver-based screen ink
Metalon® HPS-030 silver-based inkjet ink
Metalon® ICI-020 copper oxide-based screen ink

All three of these inks are low VOC water-based, and are produced by NovaCentrix and are available for purchase. Detailed data sheets can be found at www.novacentrix.com. The following table summarizes key properties of the inks.

Table 1: Properties of Metalon inks used in evaluation.

Ink Name	Material	Average particle/flake size	Loading % wt
HPS-021	Ag	2000 nm	65
HPS-030	Ag	400 nm	65
ICI-020	CuO	Proprietary	60

The substrate used for these evaluations of the silver inks is PET ST505 produced by DuPont. The substrate used for the ICI-020 substrate is Wasau Paper Exact® Index 110 lbs smooth finish.

The inks were deposited using a 325 mesh screen. Ink thicknesses were approximately 4-5 microns.

Processing and Results

Table 2. summarizes the optimized cure conditions and results for the three inks after processing with a PulseForge 3100. Since all samples were cured on a conveyor moving at 10 meters/min, the total amount of time under the PulseForge beam was 0.4 sec (ICI-020) and 0.8 sec (HPS). This is a typical processing speed in our laboratory for developmental work. However, since the PulseForge energy delivery is on the millisecond timescale and the pulse rate is synchronized to the conveyor, the total processing time is somewhat arbitrary as the conveyor can simply be sped up to further reduce the total processing time. The PulseForge 3100 can cure material up to 100 m/min. Still, 10m/min corresponds to 14.4 km of material per day. In the 12 inch configuration this is a processed area of 4,400 m^2 per day.

All of the samples were processed in open air, including the copper ink. The radiant exposure was measured using a calibrated in-house bolometer.

Table 2: Summary of processing and results

Ink	Total Processing Time *seconds*	Radiant Exposure *J/cm^2*	Sheet Resistance *mΩ/sq*
HPS-021	0.8	14	18
HPS-030	0.8	14	40
ICI-020	0.4	Proprietary	50

It is important to note that the ICI-020 ink when initially printed is comprised of non-conducting CuO and reduction agents instead of copper. The ink is converted into a Cu thin film upon processing with a PulseForge tool. Since the conversion is a transient effect, oven processing in air, even at high temperature, does not convert the film into copper. Figure 2 shows the visually dramatic effect on the film after processing.

Figure 2: Image of screen-printed ICI-020 before and after processing in open air. Note the pronounced color change after processing.

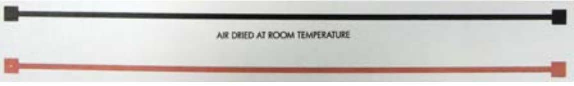

Table 3 shows a comparison of the sheet resistance of the samples undergoing both oven and PulseForge processing. The oven processing was 30 minutes @150 C. This temperature was chosen since it is the maximum processing temperature for the PET substrate. In the case of the silver-based inks, the results are similar when compared to the oven. Since the copper-based ink cannot be oven-processed to achieve conductivity, only the PulseForge tool process data is presented.

Table 4 shows a comparison of the total processing time both oven and PulseForge tool use. In all three cases, the PulseForge tool processing was over 3 orders of magnitude faster than the oven processing.

Table 3: Comparison of oven curing and PulseForge processing: Sheet Resistance

Ink	**Sheet Resistance after 30 min at 150C** *mΩ/sq*	**Sheet Resistance after PulseForge** *mΩ/sq*	**Improvement vs Oven**
HPS-021	13	18	-38%
HPS-030	50	40	20%
ICI-020	inf	50	+ inf

**** Curing conditions constrained by substrates***

Table 4: Comparison of oven curing and PulseForge processing: Processing time

Ink	**Processing time in oven at 150C** *seconds*	**Processing time with PulseForge** *seconds*	**Improvement vs Oven**
HPS-021	1800	0.8	2200X
HPS-030	1800	0.8	2200X
ICI-020	n/a	0.4	n/a

Conclusions

The PulseForge 3100 significantly increased the conductivity of three types of conductive screen inks on low-temperature flexible substrates and at processing speeds suitable for volume manufacturing. The results indicate the PulseForge tools are a viable curing platform for both developing and for manufacturing applications in advanced displays, RFID tags, batteries, and flexible photovoltaic cells.

References

[1] Schroder, K. A. et al, “Broadcast Photonic Curing of Metallic Nanoparticle Films”, NSTI May 2006

[2] Huang, J. et al, “Flash Welding of Conducting Polymer Nanofibres”, Nature Materials Letters, Vol. 3, November 2004

[3] Cote, L et al, “Flash Reduction of Graphite Oxide and Its Polymer Composite”, Journal of the American Chemical Society, 131, 11027-11032, 2009

[4] Kim, H.S., et al, “Intense pulsed light sintering of copper nanoink for printed electronics”, Appl Phys A, 5 Aug 2009

[5] Farnsworth et al, “Evaluation of Tool for Processing Metallic Conductive Inks on Low Temperature Substrates,” IMAPS 42nd International Symposium on Microelectronics, San Jose, CA, Nov 1-3, 2009