Photonic Curing Explanation and Application to Printing Copper Traces on Low Temperature Substrates

K. A. Schroder

October 2011
Abstract

NovaCentrix’s PulseForge® tools perform high temperature processing of thin films on low temperature substrates such as paper and plastic in milliseconds at speeds beyond 100 m/min in a wide web format using a unique process known as Photonic Curing. This flashlamp-based technology dries, sinters, anneals, and even modulates chemical reactions. The mechanisms and limitations of this process are presented along with an example of reducing a CuO based ink on plastic and paper.
NovaCentrix® in the Supply Chain

Printed Electronics Manufacturing

Industry product types

- Raw Materials: Ink components; Raw substrates
- Mfg Materials: Inks; Substrates
- Material Handlers: Roll-to-roll; Conveyors
- Printers
- Dryers
- Curing Tools: Ovens; Air knives; New Tech
- Device/Application: Solar; RFID; Batteries; Transistors; Displays; Packaging; Smart cards

Tool Integrators

1999: Nanoparticles
2006: Metalon® inks
2006: Novele™ substrates
2006: PulseForge® tools
2010: SimPulse™ thermal simulator

NovaCentrix Technologies and Products
Recognition and Honors

PulseForge® tools

2009: R&D 100 recipient in partnership with Oak Ridge National Laboratory
   Shipped PulseForge 3300 #001 to customer

2008: “Best Development: Manufacturing” by IDTechEx for PulseForge 3100

Metalon® ICI copper-based inks

2011: Finalist: Technology of the year by AIMCAL

2010: R&D 100 recipient
   “Best Development: Materials” by IDTechEx

2009: Labeled “Game Changer” by Printed Electronics World
Photonic Curing

- Photonic Curing was first introduced at NSTI in 2006.
- It is the use of a flashlamp to transiently heat a thin film to high temperature on a low-temperature substrate without damage.
- First used to sinter nanosilver and nanocopper inks on plastic and paper.

Photonic curing is fundamentally a transient thermal process and includes sintering, annealing, drying, crystallization, polymerization, chemical reaction initiation and modulation, dopant drive-in, degasification, etc.

- It has become a key enabler to printed electronics as it has enabled high speed processing of high temperature materials on cheap low temperature substrates such as plastic and paper.
- Technology has been scaled to process roll to roll materials in a wide web format at speeds up to 100 m/min.
Inspired by a camera flash which has properties of:

- Moderate power: 2 kW/cm²
- Low energy: 1 J/cm²
- Suitable for certain types of nanoparticle processing on low temperature substrates
PulseForge®: Simple Beginnings
PulseForge®: Simple Beginnings

Inspired by camera flash which has properties of:
- High power: 2 kW/cm²
- Low energy: 1 J/cm²
- Suitable for certain types of nanoparticle processing on low temperature substrates

But camera flash needs improvement for use in printed electronics:
- Poor controllability
- Limited power and energy
- Erratic output
- Not well suited for use in roll-to-roll production

New Technology needed to be developed beyond current “industrial” systems.
- Needed the control of laser processing, but the economics of oven processing.

The result was PulseForge!
PulseForge® Tools

Designed and built specifically to solve the thermal problem. The tools use intense pulsed light to heat functional inks and thin films without damaging temperature-sensitive substrates like plastic films and paper. This process is known as Photonic Curing.

- Designed for development and production use.
- Developed in cooperation with Oak Ridge National Laboratory.
- > 10 US and international patents issued or pending relating to using flash lamps to sinter nanometal inks on low temperature substrates as well as other processes enabled by this technology.

Materials processing

Drying
Sintering
Annealing
Reacting
Typical Thermal Profile

- High temperature processing removes excess solvent and enhances sintering.
- Substrate is undamaged.

Conditions:
1 \( \mu \)m Ag Film on 150 \( \mu \)m (6 mil) PET
Radiant exposure: 1 J/cm\(^2\)
Pulse length: 300 \( \mu \)s
## Traditional Processing Methods

### Ovens
- **Positives**
  - Wide area of processing
  - Uniformity
- **Negatives**
  - Cure temperature is limited by the substrate (e.g. PET ~150°C).
  - Curing times are long: >minutes

### Lasers
- **Positives**
  - High power densities
  - Spatial selectivity
- **Negatives**
  - Small exposure area requires rastering and registration
  - Fixed wavelength
  - Pulse lengths are too short
  - Cost at production scale
Combining Desired Processing Attributes

**PulseForge**

- Wide area of processing
- Uniformity
- Cure temperature is not limited by the substrate (e.g. PET ~150°C).
- Curing times are short: ~milliseconds

- High power densities
- Selective material processing
- Large exposure area does not require rastering or scanning – maskless!
- Broadband adjustable spectrum
- Tunable pulse lengths from microseconds to milliseconds
- Economical production scale: >1m²/sec
A thin film on a low temperature substrate can be processed at temperatures far beyond the maximum working temperature of the substrate.

- If the duration at high temperature is short enough, the substrate is undamaged.
- This requires both rapid heating and rapid cooling.
  - Rapid heating provided by pulsed light.
  - Rapid cooling provided by the thermal mass of the substrate.

Many thermal processes are Arhenius in nature, i.e. the curing rate is related to the exponential of the temperature.

→ This submillisecond process often outperforms a 10 minute process in an oven!

- This process naturally lends itself to high speed roll to roll processing.
Transient Curing Conditions

High temperature processing can be performed on a low temperature substrate using a transient heating process. We have established the requirements for optimal high temperature processing on a low temperature substrate.

1. $x_f \ll x_s$ The thin film is much thinner than the substrate.
2. $t_p \ll \tau_s$ The substrate doesn’t thermally equilibrate during heating.
3. $\tau_f \ll t_p$ The thin film is in thermal equilibrium during heating.

These are ideal conditions, much can still be done with nonideal processing.

\[ \tau_i = c_i \rho i x_i^2/4\kappa_i \]
Process Limitations

<table>
<thead>
<tr>
<th>Limitation type</th>
<th>Processing limit</th>
<th>Symptom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>Substrate heated beyond maximum working temperature after thermal equilibrium</td>
<td>Substrate warping</td>
</tr>
<tr>
<td>Power (1)</td>
<td>Maximum temperature reached is greater than the gasification temperature of the substrate</td>
<td>Clean film ablation</td>
</tr>
<tr>
<td>Power (2)</td>
<td>Gas generation within the film</td>
<td>Cohesive failure of the film</td>
</tr>
</tbody>
</table>

- There are three types of generic thermal limitations with Photonic Curing.
Cost Reduction Using Copper Inks

• Good
  – Cu costs 100X less than Ag
  – Cu has 90% of the conductivity of Ag

• Bad
  – True Cu inks want to oxidize, especially nanoparticle inks
  – Stable Cu inks are expensive, outweighing cost benefits

• New Approach
  – Instead of fighting oxidation, begin with particles in their terminal state: fully oxidized.
  – CuO ink formulation:
    • Nano CuO
    • Reduction agent
    • Water and ethylene glycol
  – No conductivity when printed
  – Converts to Cu during PulseForge processing.
Converting the CuO into Cu

- The reducers in the copper oxide ink don’t work at temperatures below the decomposition temperature of PET (150 °C). → An oven doesn’t work.

- An intense pulse from a PulseForge tool is able to heat the printed trace to a high enough temperature to gasify the reducers making them much more active and thereby modulating the redox reaction.

- Similar to the sintering process, the high temperature reduction is transient, so Cu films can be formed on low temperature substrates at roll to roll processing speeds.

Solvent and reducers escape

CuO and reducer - ~500 nm thick

Densification and reduction

Final trace is highly conductive copper
Case Study: Inkjet CuO on PET

Material System
Ink material: Metalon ICI-003CuO inkjet
Substrate: Coated PET w/ 150 °C max working temp
Print method: Epson C88+ Photo Stylus
Print passes: 1 @ ~0.5 micron total thickness

<table>
<thead>
<tr>
<th>Cure Condition</th>
<th>PulseForge</th>
<th>SEM - Uncured</th>
<th>SEM - Cured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>NA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>7 millisec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resulting sheet resistance</td>
<td>110 mΩ/sq</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comments:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Copper inkjet!</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• 4x bulk Cu resistivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Processed Cu ink in ambient air conditions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Resulting sheet resistance: 110 mΩ/sq
Case Study: Screen CuO on Paper

Material System
- Ink material: Metalon ICI-020 CuO screen print
- Substrate: Standard 110 lb. cardstock
- Print method: 325 mesh screen

Cure Condition | PulseForge
---|---
Temperature | NA
Time | 5.5 millisec
Resulting sheet resistance | 40 mΩ/sq
Comments:  
- Cure speed 30 fpm in ambient air conditions
- Cannot be cured in ordinary oven
**PulseForge® Tools: Commercial Implementation**

**Use**
- Development and Manufacturing

**Target Applications**
- Energy: PV, batteries, capacitors
- Communications: displays, sensors
- Lighting, flexible circuits

**Performance**
- Broadly applicable to organics, metals, and semiconductors
- Reel to reel processing speeds over 100 meters/min
- Drop-in with existing material handling systems

**Key tool attributes**
- Highly-configurable pulse conditions
- Integrated thermal simulation software
- Rapid-change lamp system
- Scalable design for matching width requirements – up to 2 meters wide.

![PulseForge 3300](image)
Summary

• Photonic curing is the high-temperature thermal processing of a thin film using pulsed light from a flashlamp.
• We have established three transient curing conditions for optimal high-temperature processing of a thin film on a low-temperature substrate using this process.
• A high speed commercial photonic curing system, called PulseForge, has been developed with 10 process variables to exploit this effect.
• The basis of PulseForge tools is the use of intense pulsed light to briefly heat the film without affecting the substrate.
  – Reduces or even eliminates the need for an oven to cure many materials
  – The process is able to cure materials that cannot ordinarily be thermally processed in air such as sintering a copper particle film
  – The process is broadcast by nature and maskless, with no need for registration
• The system contains an integrated thin film stack thermal simulator with predictive capability.
• PulseForge tools often outperform ovens and are much more scalable than laser processing. Low temperature materials such as PET and paper are now feasible substrates for high-performance printed electronics applications.
• The transient nature of the process allows for the high temperature modulation of chemical reactions on low temperature substrates. An example of this is the formation of very low cost copper film using CuO and reducers in the ink.
Thank You

Contact us with questions or for samples processing

www.novacentrix.com