Developments in Printed Electronics

Processing - Photonic Curing
Materials - Copper Oxide Reduction Inks
Simulation - Numerical Thermal Processing

Stan Farnsworth VP Marketing Oct 2011
NovaCentrix® in the Supply Chain

Printed Electronics Manufacturing

Industry product types

- Nanoparticles
- Metalon® inks
- Novele™ substrates
- PulseForge® tools
- SimPulse™ thermal simulator

Commercial Product Release

- 1999
- 2006 (inks)
- 2009 (substrate)
- 2007 (tools)
- 2010 (simulation)
Printed Electronics

The Next Generation of Energy and Function

Solar cell  |  Battery  |  RFID tag  |  OLED lighting

>$50B  Projected component value in 2020 across printed electronics*.

> 2500  Number of organizations involved in developing new applications*

* IDTechEx (www.idtechex.com)
Printed Electronics

Advanced Functionality

- Solar cell
  NanoSolar

- Battery
  Solicore, Inc.

- RFID tag
  PolyIC

- OLED lighting
  GE

By the m²:

Clemson’s Sonoco Institute
Achieving high performance from printed materials requires post-processing at elevated temperatures.

Plastic and paper substrates can’t accommodate those temperatures and maintain low cost.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Temp</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>150°C</td>
<td>$0.10/ft²</td>
</tr>
<tr>
<td>Polyimide</td>
<td>375°C</td>
<td>$1-$20/ft²</td>
</tr>
</tbody>
</table>
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 fragile temperature-sensitive substrates like plastic films and paper.

- Designed for development and production use.
- Developed in cooperation with Oak Ridge National Laboratory.
- **Patented Process: USPTO Patent # 7,820,097.**

Materials processing

- Drying
- Sintering
- Annealing
- Reacting
PulseForge®: Simple Beginnings
PulseForge®: Simple Beginnings

Inspired by camera flash which has properties of:
- High power: 2 kW/cm^2
- Low energy: 1 J/cm^2
- 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

The need was to create a tool based on these principles that could be used for industrial-scale processing as well as for lab-scale development.
PulseForge® Toolset
PulseForge® Tools: Commercial Implementation

Use
- Development and Manufacturing

Sample Tool Performance
- Peak Delivered power: 14 Megawatts/pulse
- Minimum Pulse: 25 micro seconds
- Pulse Frequency: kHz
- Cooling: Water-cooled
- Lamps: No tools required
- Pulse Settings: Touch-screen
- Line Speeds: >100 Meters/min

Target Applications
- Energy: PV, batteries, capacitors
- Communications: displays, sensors
- Lighting, flexible circuits
- Broadly applicable to organics, metals, and semiconductors
- Process speeds over 100 meters/min
- Drop-in with existing material handling systems
Typical Single-Pulse Thermal Profile

Numerical Simulation

- Peak temp >1000 C
- Substrate < 150 C @ 8 ms
- Thermal equilibrium @ 35 ms (90C)

Conditions:
1 µm Ag on 150 µm (6 mil) PET
Radiant exposure: 1 J/cm²
Pulse length: 300 µs

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

Material Characteristics
- Thermal / physical properties of ink and substrate
- Film/ ink thickness
- Particle morphology
- Substrate composition and thickness
- Barrier or intermediate layers

Tool Adjustability Requirements
- Pulse energy/ amplitude
- Pulse duration
- Impinging wavelengths
- Number of pulses
- Speed of pulses
- Other parameters

Nanoparticle inkjet - ~500 nm thick
Micron flake screen print - ~5-30 microns thick
Metalon® Inks: Low Cost and Available

Water-based, low VOC, with nanoparticle and flake materials

Priced as low as 1/20 vs. competing inks

Next-day delivery in most cases

Can be used with low-cost consumer printers

Options for any print method
  – Inkjet, screen, flexo, gravure

Silver and copper are standard, can be customized
Case Study: Screen Ag on PET

Material System
- Ink material: Metalon® HPS-021 Ag screen print
- Substrate: PET w/ 150 °C max working temp
- Print method: Drawdown, #10 bar
- Coating weight: ~0.003 g Ag/cm² (~ 3 micron thick assuming 100% dense)

<table>
<thead>
<tr>
<th>Cure Condition</th>
<th>Oven</th>
<th>PulseForge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>150 C</td>
<td>NA</td>
</tr>
<tr>
<td>Time</td>
<td>30 minutes</td>
<td>4 millisec</td>
</tr>
<tr>
<td>Resulting sheet resistance</td>
<td>18 mΩ/sq</td>
<td>18 mΩ/sq</td>
</tr>
</tbody>
</table>

Comments:
- Much faster curing with PulseForge tools
- Cure speed 30 fpm
Material Set-up

- Ink: Dupont 5025

- Substrates
  - Melinex 329 (white)
  - STS 505 PET (clear with black background for contrast)

- Ink thickness when properly cured: ~10 microns

- Ink conductivity when properly cured: <10milliOhms/sq

- Cure Conditions:
  - Conventional: ~140C, 10-30 minutes
  - PulseForge tool process: ~500C, ~1 millisecond
Cost Reduction Using Copper Inks

• Good
  – Cu costs 60X 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.
PulseForge Processing of CuO on PET (Simulation)

- Peak temperature is high enough to rapidly reduce CuO while reducers are in the gaseous phase.
- The short time scale of processing combined with solvent and reducer evaporation prevent substrate from getting too hot.
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.

- High temperature reduction is both transient and adiabatic, 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-003 CuO 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>
</tbody>
</table>
| Comments:      | • Copper inkjet!  
                • 4x bulk Cu resistivity  
                • Processed Cu ink in ambient air conditions | | |

Resulting sheet resistance: 110 mΩ/sq

Comments:
- Copper inkjet!
- 4x bulk Cu resistivity
- Processed Cu ink in ambient air conditions
## Case Study: Screen CuO on Paper

### Material System
- **Ink material:** Metalon ICI-021 CuO screen print
- **Substrate:** Standard 110 lb. cardstock
- **Print method:** 165 mesh screen

<table>
<thead>
<tr>
<th><strong>Cure Condition</strong></th>
<th><strong>PulseForge</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>NA</td>
</tr>
<tr>
<td>Time</td>
<td>5.5 millisec</td>
</tr>
<tr>
<td>Resulting sheet resistance</td>
<td>20 mΩ/sq</td>
</tr>
</tbody>
</table>

### Comments:
- Cure speed 30 fpm in ambient air conditions
- Cannot be cured in ordinary oven
PulseForge® Simulation: SimPulse™

• SimPulse was developed to simulate and predict the results of PulseForge tool processing.
  – It acts as a quantitative visualization tool
  – Accelerates process development

• Inputs:
  – The interface is nearly identical to an actual PulseForge tool
  – Graphically build a thin film stack of any number of layers and materials
  – Enter the desired PulseForge conditions
  – Then hit “Simulate” for near-instant results

• Output:
  – Graphical display of the stack Temperature versus Time
  – Can provide temperature at any location in the stack, at any time during or after the exposure

• Availability
  – Ships installed on standard-configuration PulseForge tools
  – Will soon be available through a portal on our website.
The SimPulse User Interface has 3 panels:

- The Film Editor
- The Pulse Editor
- The Process Simulator
The SimPulse Film Editor allows a user to graphically build a thin film stack of materials:

- Any number of layers may be specified.
- Any number of materials may be specified:
  - Standard materials
  - From other databases
  - User defined
- Cooling at the top and bottom surfaces is specified:
  - Natural convection
  - Forced convection
  - Liquid
The SimPulse Pulse Editor allows a user to customize the input power delivery to the stack on a microsecond timescale including:

- Radiant power
- Pulse duration
- Advanced multipulse and ramp heating profiles
- Allows user to control the temperature in each portion of the thin film stack.
SimPulse™ Process Simulator

The SimPulse Process Simulator displays the temperature at each layer interface versus time both during and after heating.

- Predicts the actual PulseForge performance system under the conditions provided by the Film and Pulse Editors.
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.
Special thanks to Showa Denko K.K. for cooperation

Shoko Co., LTD is official PulseForge tool representative

Contact our partners or us directly with questions or for samples processing

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