LOW TEMPERATURE PHOTONIC SINTERING FOR PRINTED ELECTRONICS

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Topics

- Introduction
- Significance of nanotechnology
- Conductive inks
- Pulsed light for sintering
- Reel-to-reel challenges
- Conclusions
Preamble: Clarke’s third law

“Any sufficiently advanced technology is indistinguishable from magic”

Early alchemists tried to convert base metals to gold.

We are forming solid metals from ink using light.

King Solomon’s tablet partially covered with gold

Printed gold traces on PET
Current Printed Circuit Process

- Current process for printed electronic system requires multiple process steps
- They do not lend themselves to Reel-to-reel Systems
  - Flexible substrates
  - Low Temperature Substrates
  - Complex steps
- A simpler process would be to print conductive traces and cure to form conductive traces

Comparison of Standard Printed Circuit Manufacture and Photonic Sintering
Sintering

Definition:
- Sintering is a method for making objects from powder typically **below its melting point**
- Traditionally use heat, pressure and time

History
- 1906: first patent on sintering using vacuum by A. G. Bloxam.
- Decades of development with around 640 patents

Some current methods of sintering:
- Sintering ovens
- Arc discharge
- Laser
- And now: **pulsed light**
Nanoparticles

- **Definition:**
  - Particles that have a size between 1 nm to 100 nm are referred to as "nanoparticles"

- Diameter of a hydrogen atom is about 0.1 nm

- Nanotechnology creates and uses structures that have novel properties because of their small size.

Classic nanoparticle
Buckminsterfullerene C60
Nanoparticles

- All materials have basic properties
  - Melting point, light absorption (color) etc.
  - Governed by laws of particle physics

- These are independent of size
  - Melting point for a gram of copper is the same as for a kg of copper. It still looks like the same material

- Once materials become around the size of 1 to 100 nanometers quantum effects becomes significant
  - Optical absorption characteristics change: quantum dots
  - Opens up new possibility of sintering at significantly lower temperature when compared to bulk material

- When particle size becomes smaller than the wavelength of light plasmon effects play a role in its absorption spectra

Metallic gold and gold nanoparticles in ruby glass
Melting Point Depression

- Melting point depression is a feature of metal nanoparticles where the melting point of the particle is lower than that of bulk based on the size of the particle.

- This effect can be explained by classical physics as the surface area to volume ratio of the material is changed.

- As surface area to volume for material becomes large a phenomenon called “melting point depression” occurs. The Gibbs-Thomson relation is shown below:

\[ T_M(d) = T_{MB}(1 - \frac{4\sigma_{sl}}{H_f \rho_s d}) \]

Where:
- \( T_{MB} \) = bulk melting temperature
- \( \sigma_{sl} \) = solid liquid interface energy
- \( H_f \) = bulk heat of fusion
- \( \rho_s \) = density of solid
- \( d \) = particle diameter

Melting point Gold Clusters
Absorption Spectra

- As particle size becomes smaller their absorption characteristics change
  - Example: quantum dots

\[ E = \text{Extinction} \]
\[ N_A = \text{aerial density of nanoparticles,} \]
\[ a = \text{radius of the metallic nanosphere,} \]
\[ \varepsilon_m = \text{dielectric constant of the medium surrounding the metallic nanosphere} \]
\[ \lambda = \text{the wavelength of the absorbing radiation,} \]
\[ \varepsilon_i = \text{imaginary portion metallic nanosphere’s dielectric function,} \]
\[ \varepsilon_r = \text{real portion metallic nanosphere’s dielectric function.} \]

\[ E = \frac{24\pi^2 N_A a^3 \varepsilon_m^{3/2}}{\lambda \ln(10)} \left[ \frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2} \right] \]

Mie theory estimation of the extinction of a metallic sphere in the dipole limit

Quantum dots---same material (different sizes have different colors)

UV-visible extinction spectra of Ag SL PPA
The Nanoparticle Advantage

- Combination of melting point depression and absorption characteristics change mean that photonic energy can cause sintering, i.e., the bonding of nanoparticles together to form bulk metal.

- Once sintering has taken place the material behaves like bulk material and loses the nanoparticle characteristics (we want this).

- If photonic energy is too high then the metal can evaporate (we don’t want this).

Photonic sintering of Cu nanoparticles on teflon showing unsintered, partially sintered, sintered and blow-off regions (2X mag)
Flash Lamps

- Xenon flash lamps have a broad spectrum of light from deep UV to IR.
- Typically used for curing and sterilization where high photon energy is required.
- When xenon gas is broken down due to a high energy field it goes from being an insulator to a conductor.
- Excitation and recombination of ions within the arc plasma creates light.
- The envelope used can determine the spectral content of the lamp.
- Lamps can explode due to excess energy:
  - Typically operate at 10% of explosion energy
  - Equation for explosion energy ($E_{\text{exp}}$) as a function of pulse duration time ($t$), arc length ($l$) and diameter of lamp ($d$).

$$E_{\text{exp}} = 12 \cdot l \cdot d \cdot \sqrt{t}$$
A simplified drawing of the electronics is shown below.
A high voltage power supply is used to charge a capacitor.
An inductor is used to shape the pulse as the capacitor discharges.
A trigger circuit is used to generate a high potential across the lamp to cause the gas inside the lamp to ionize and create a conductive path.
Once ionized the lamp conducts and the energy stored in the capacitor flows through the lamp creating the flash.
Once the capacitor is discharged the gas inside the lamp stops ionizing and becomes an insulator.
Pulse shape can be changed by changing the number of caps and inductors in the system.
Pulse energy can be controlled by adjusting the voltage.
Pulse Characteristics

- Energy = Watt-seconds

- Peak power = \( CV^2/2\)/T

- Pulse duration is defined as the half max width for the current graph (T)

- Lamp intensity correlates well with lamp current.

- Energy per pulse is area under the V and I

- By increasing the voltage we can increase the peak and total energy per pulse.
Pulsed vs. Continuous

- If we try to expend 100 Joules of energy we can do it in two ways
  - 10 W lamp for 10 seconds or
  - 1 MW pulse for 100 microseconds.
- Continuous systems like mercury or halogen lamps cannot deliver this kind of peak power.
- High peak power means the system is more efficient at delivering useful energy
- Intensity attenuates as it penetrates into a material so peak power phenomenon allows for deeper penetration depths
- Shorter pulse duration means that the process can take place quicker
- Pulsed is instant on-off. It is harder to do that with continuous systems
- Pulsed systems can be frequency adjusted to allow time for cooling
Cooling

- If you dissipate 3kW in a system where energy is predominantly electrical you have to consider cooling.

- Options for lamp cooling rough guide
  - Ambient
  - Forced Air
  - Liquid

- Water and electricity do not mix

- Forced air or water cooling is required for higher peak power.
Advantages
Pulsed Xenon light for Photonic Sintering

- **High intensity**
  - Can achieve results faster and with fewer pulses

- **Non-contact Process**
  - Lamp units are relatively small, can be retro fitted to an existing process
  - Is easy to maintain (no moving parts)

- **Low temperature**
  - Produces high energy pulsed light which has a very short duration (few us to few ms)
  - Have comparatively high conversion efficiency.
  - This allows the use of low temperature substrates like paper or plastic

- **Simple to implement and use**
  - No scanning laser, no rolling plasma, no oven
  - Pulse rate can be synchronized with the system
  - No special requirements for process, e.g. vacuum, temperature or gasses

- **Fast**
  - Sintering occurs in fractions of seconds, does lend itself to roll-to-roll

- **Scalable**
  - Faster process speeds can have multiple systems operating in synchrony

- **No waste**
  - No chemicals used

- **Flexible**
  - Broad spectrum light means that different inks/substrates can be processed with the same system.
Conductive Inks

- There are many types of conductive inks that can benefit from photonic sintering
  - Copper nanoparticles
    - May have core/shell structure
    - May have reduction agents in the carrier
    - May require photo reduction by UV
  - Silver ink
    - Flakes (not nanoparticles, but photonics can remove carrier)
    - Silver nanoparticles
  - Semi-conductive inks
    - For photovoltaics, electronic components
  - Tin- and gold-based inks

- Ink particle size, carrier medium, substrate, deposited thickness, all play a role in defining the required parameters for effective sintering
Functional Inks

- Often use of printed electronics demands a range of functions defined by their use
  - Resistivity is the most common requirement
  - Transparency for touch panels
  - Adhesion
  - Flexibility
  - Reflectivity

- In the standard printing world these functions are not required

- Accuracy of the print process in terms of layer thickness and placement is more critical than for standard printing
  - Layer thickness relates with resistance $R = \rho \frac{I}{A}$
  - Poor accuracy may lead to shorts or open circuits
Silver Inks

- Silver inks are well suited to photonic sintering
  - Both silver and its oxide are conductive
  - Formulation and manufacture of silver nano inks are easier and more prevalent
  - Their operational window is large
  - Their size can be tightly controlled
  - They can show improvement in their functionality with multiple pulses (contrary to the concept of nanoparticle advantage)

SEM of Silver Nano particle
5-6nm in size

AG Film on PET
Silver Ink Tests

- We have the greatest success with photonic sintering of silver.
  - Silver requires lower energy per pulse and can be flashed a number of times to bring the resistivity down. This means that stitching problems can be effectively mitigated.
  - It seems like total incident energy is the dominant factor with the majority of inks tested.
  - Silver typically has some resistance before sintering and so unsintered areas do not cause open circuits.

![Resistance change evaluation graph](image)

- Resistance change evaluation @ 30 HZ setting / 550J stored - 250 usec clip for energy deposit duration

- Conductive particles
- Carrier
- Substrate
- Carrier removed with light
Copper Inks

- Copper is harder to sinter than silver
  - Copper is conductive but copper oxide is not
  - Copper oxidizes easily
  - Often requires a core shell design to protect it
  - Tight control of particle size can be harder
  - Operational window between sintered and blow off is small
  - Expresses nanoparticle advantage prominently and does not lend itself to secondary pulse
  - Stitching issue may require more energy to do the job

- Successfully sintered copper with good results
- Photonic sintering may have advantage in photo reduction of the oxide
Copper Tests

- We see resistivity change by changing the energy of the lamp and the pulse width.
- Increase in resistance is due to blow off.
- Good resistance values were available.
- Shorter pulse widths require less energy to achieve the same results.
- Interesting that it is not a total energy phenomenon. Efficiency does fall off with the duration of the pulse.
- Showing that for this ink that more efficient system is one that use the shortest pulse and requires less energy.
Stitching

- Stitching is important for roll-to-roll applications
  - If pulse rate is too slow for the reel-to-reel speed then we get banding with regions of unsintered area and regions of sintered area.
  - Impact of the nanoparticle advantage needs to be considered
  - Overlapped regions may impact uniformity requirements
  - Use of close proximity mask may be required
  - Accurate control of flash may be required
Substrate Types

- Substrates play a vital role in the photonic sintering domain.
  - Paper can absorb some of the carrier and can help with adhesion and sintering.
  - PET can have adhesion issues, can warp with too much energy.
  - Metal substrates like aluminum can be hard to sinter as it acts like a heat sink in some cases; significant for silver, not so much for copper.
  - Some substrates do not allow the ink to dry effectively and this can negatively impact sintering.
Different kinds of printing processes can be used for photonic sintering. Choice determined by desired thickness and feature size.
Reel-to-Reel Application

- Reel-to-reel applications have unique requirements
  - Process speeds 5ft/min to 100s ft/min
    - Faster throughput increases efficiency and reduces costs
    - Synchronization is important
  - Web based systems demand higher reliability
    - Down time and failure generates waste
  - Web size can vary
  - Flexibility is required
    - Different inks, different substrates, different applications
  - Functional uniformity of result is important.
    - Tolerant to ink thickness and printing process
## Process speeds based on printing technology

<table>
<thead>
<tr>
<th>Basic Principle of Ink Separation on the Image Carrier</th>
<th>Resolution</th>
<th>Ink Film Thickness</th>
<th>Printing Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen</td>
<td>50 µm</td>
<td>3 - 60 µm</td>
<td>8 m/s</td>
</tr>
<tr>
<td>Inkjet</td>
<td>20 µm</td>
<td>0.05 – 0.5 µm</td>
<td>2.5 m/s**</td>
</tr>
<tr>
<td>Flexography</td>
<td>20 µm</td>
<td>0.5 - 2 µm</td>
<td>5 m/s</td>
</tr>
<tr>
<td>Gravure</td>
<td>15 µm</td>
<td>0.5 - 8 µm</td>
<td>15 m/s</td>
</tr>
</tbody>
</table>

* Maximum speed based on what is used in traditional printing applications ** for 600 x 600 dpi

Source: WMU CAPE
Process Speed based on Photonic Technology

- For photonic sintering process speeds are defined by the flash rate, energy per pulse and number of flashes required.
  - For optimal performance the lowest energy required with the shortest pulse needs to be identified for the process.

- These define the total energy demand of the system and the required cooling for safe operation of the lamp.
  - The lower the energy per pulse the faster the lamp can be flashed.

- Flash lamp systems can be scaled to include multiple sources to keep up with process speed.

- Example values for a 16" lamp housing is 12" x 1" optical footprint with a pulse rate of 3 Hz = 15 ft/min web speed.

![Diagram showing optical footprint, flow speed, overlap, and flow too fast for pulse rate banding.](image-url)
Integration into Process

- In most cases integration of a photonic sintering system can be done as a retrofit to an existing print process
  - Systems are typically modular
  - Lamp system has a small footprint
  - Indexing is a standard requirement for print process and this can be used to synchronize lamps
- May require additional sensors for monitoring the desired ink function
- May require redundant systems for easy maintenance and correction for lamp failure
The technology is well suited to small scale systems like ink jet printing and gravure printing.

- There are many lamp designs that can lend themselves to a retro fit for a staged system.
- Typically a lot more flexibility in speed, so can be accomplished with a single lamp solution.
Products

- Lowest cost static sintering solution
  - Sinteron 500
- More flexible, more powerful system
  - Sinteron 2000
- Small scale linear stage
  - LS-845
- Reel-to-reel prototype system
  - Under development
Conclusions

- Photonic sintering:
  - Works with many conductive nanoparticles for printed electronics needs
  - Requires high energy which can be generated by a flash lamp
  - Fast, compact and cost effective alternative to ovens
  - Easy retrofit to existing process for roll to roll deployment
  - Needs to be flexible to work with various ink formulations
  - Should be scalable for different process speeds

- Reel-to-reel offers unique challenges for pulsed light.

- Xenon is actively involved in creating synergies between researchers, developers and manufacturers for printed electronics