

Photonic Sintering of Silver for Roll-to-Roll Printed Electronics

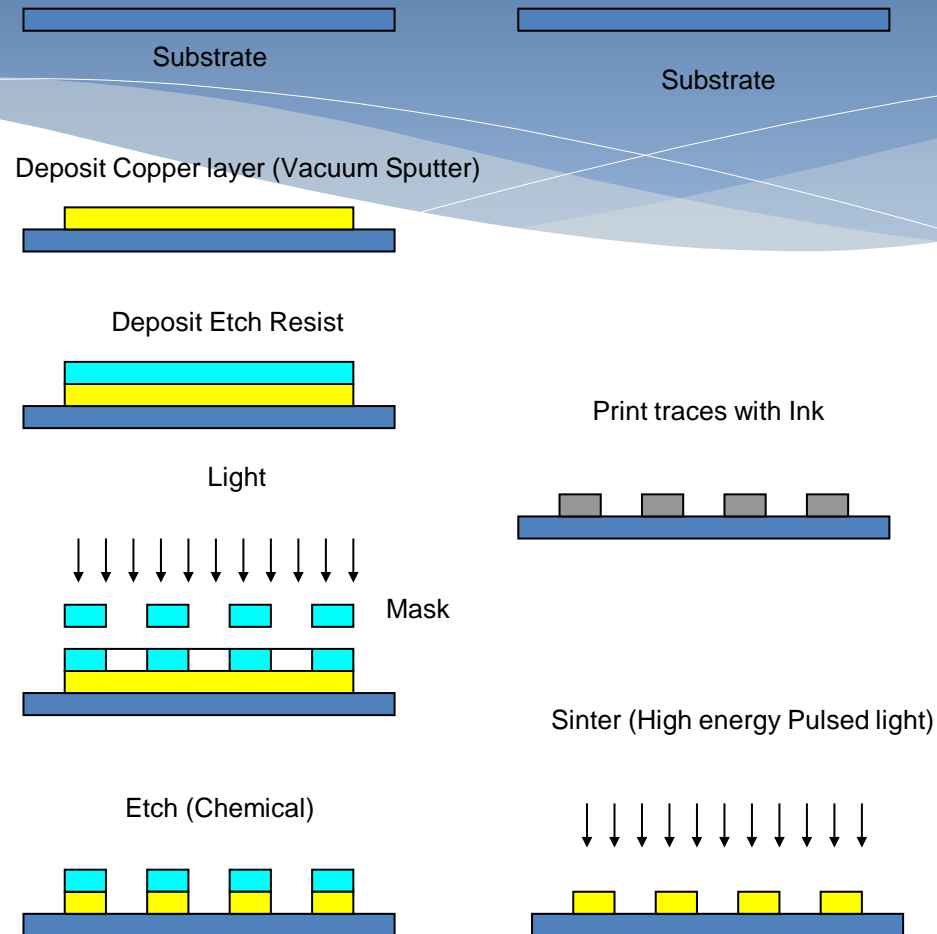
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Topics

- * Introduction
- * Significance of nanotechnology
- * Conductive inks
- * Pulsed light for sintering
- * Reel-to-reel challenges
- * Conclusions

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**



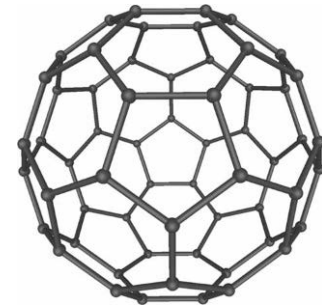
Vacuum sintering oven



Xenon arc lamp on a reel-to-reel system at Western Michigan University (USA)

Nanoparticles

- * Definition:
 - * Particles that have a size between 1nm to 100nm 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.



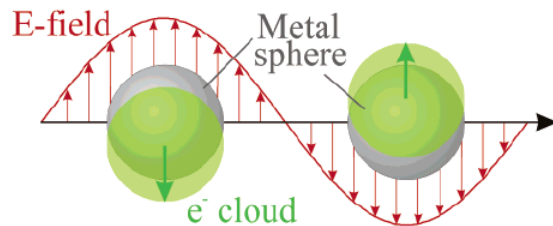
Classic nanoparticle
Buckminsterfullerene C60

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



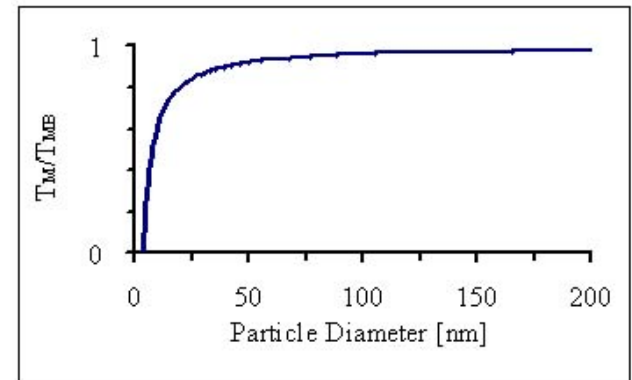
Metallic gold and gold nanoparticles in ruby glass



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:

$$T_M(d) = T_{MB} \left(1 - \frac{4\sigma_{sl}}{H_f \rho_s d} \right)$$



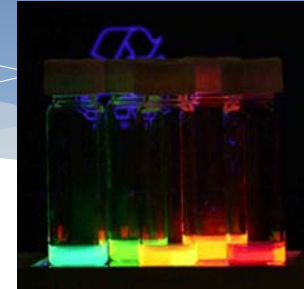
Melting point Gold Clusters

Where: T_{MB} =bulk melting temperature
 σ_{sl} =solid liquid interface energy
 H_f =bulk heat of fusion
 ρ_s =density of solid
 d =particle diameter

Absorption Spectra

* As particle size becomes smaller their absorption characteristics change

* Example: **quantum dots**



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

E = Extinction

N_A = aerial density of nanoparticles,

a = radius of the metallic nanosphere,

ϵ_m = dielectric constant of the medium surrounding the metallic nanosphere

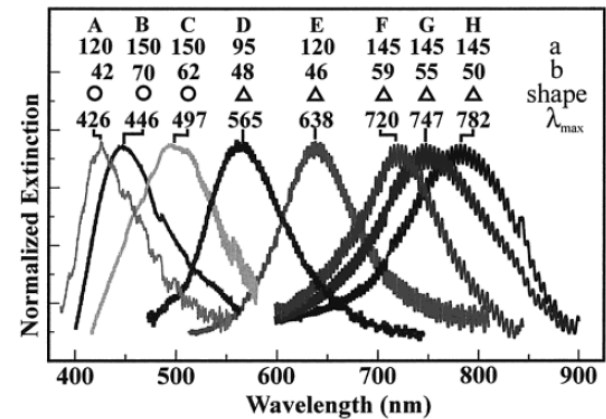
λ = the wavelength of the absorbing radiation,

ϵ_i = imaginary portion metallic nanosphere's dielectric function,

ϵ_r = real portion metallic nanosphere's dielectric function.

$$E = \frac{24\pi^2 N_A a^3 \epsilon_m^{3/2}}{\lambda \ln(10)} \left[\frac{\epsilon_i}{(\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2} \right]$$

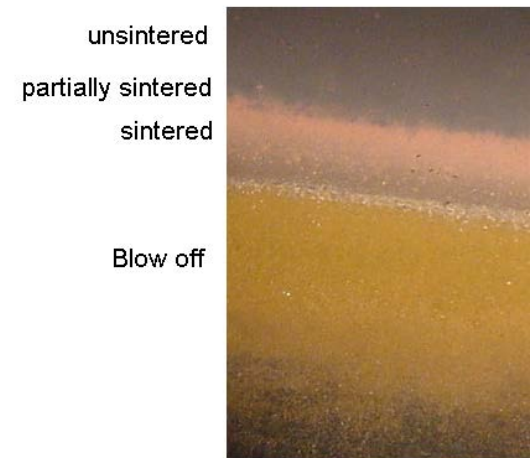
Mie theory estimation of the extinction of a metallic sphere in the dipole limit



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)

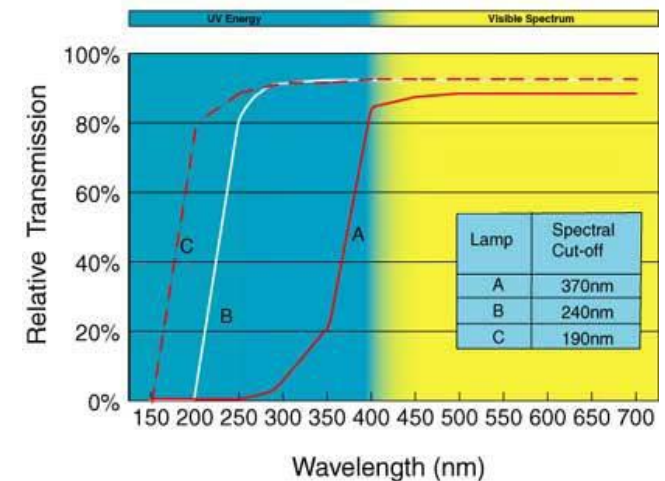
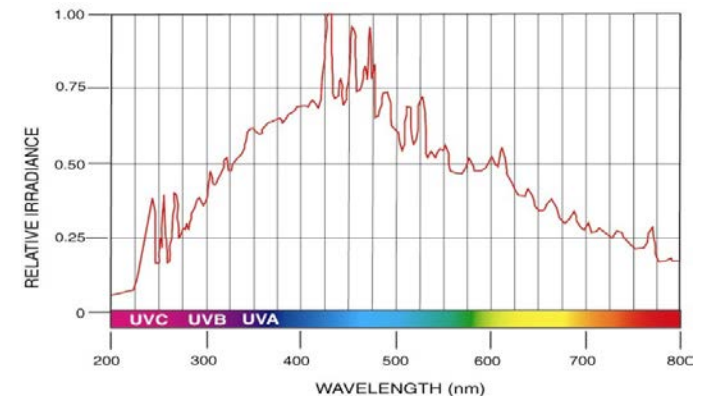


Photonic sintering of Cu nanoparticles on teflon showing unsintered, partially sintered, sintered and blow-off regions (2X mag)

Flash Lamps

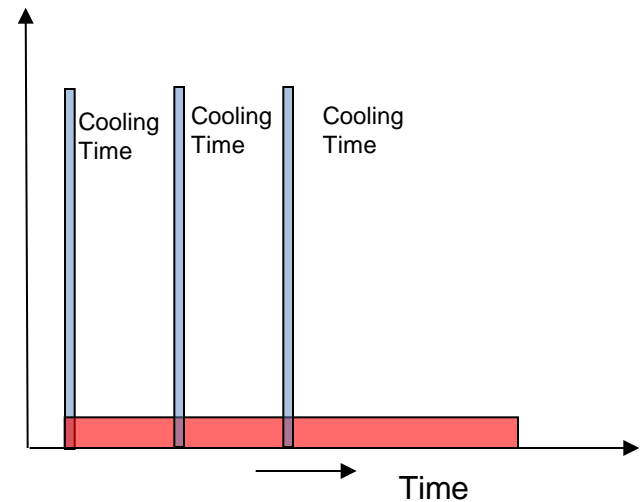
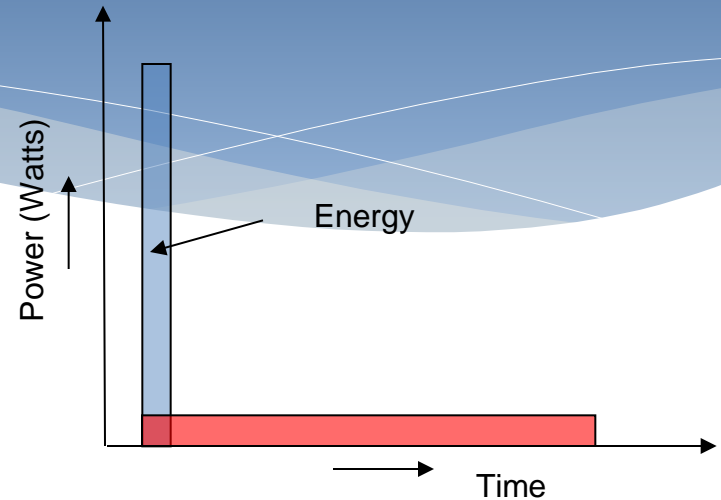
- * Xenon flash lamps have a broad spectrum of light from deep UV to IR.
- * Typically used for curing and sterilization where high photon energy is required
- * When xenon gas is broken down due to a high energy field it goes from being an insulator to a conductor
- * Excitation and recombination of 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_{exp}) as a function of pulse duration time (t), arc length (l) and diameter of lamp (d).

$$E_{exp} = 12 \cdot l \cdot d \cdot \sqrt{t}$$



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



Advantages

Pulsed Xenon light for Photonic Sintering

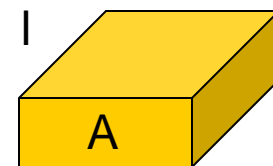
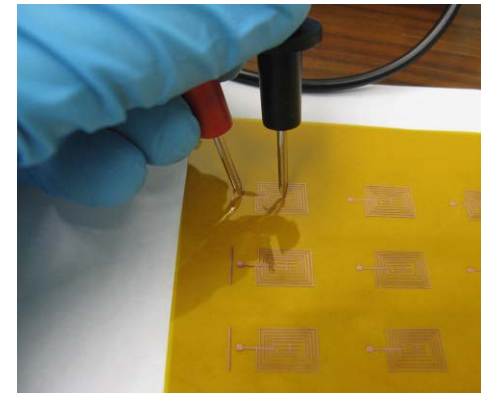
- * High intensity
 - * Can achieve results faster and with fewer pulses
- * Non-contact Process
 - * Lamp units are relatively small, can be retro fitted to an existing process
 - * Is easy to maintain (no moving parts)
- * Low temperature
 - * Produces high energy pulsed light which has a very short 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 type 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

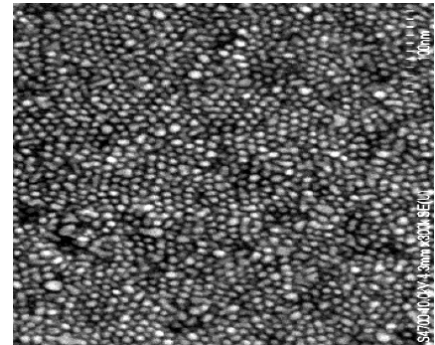
Functional Inks

- * 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 $R = \rho l / A$
 - * Poor accuracy may lead to shorts or open circuits

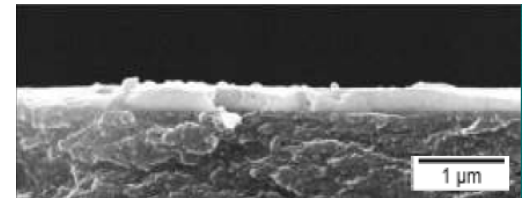


Silver Inks

- * 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)



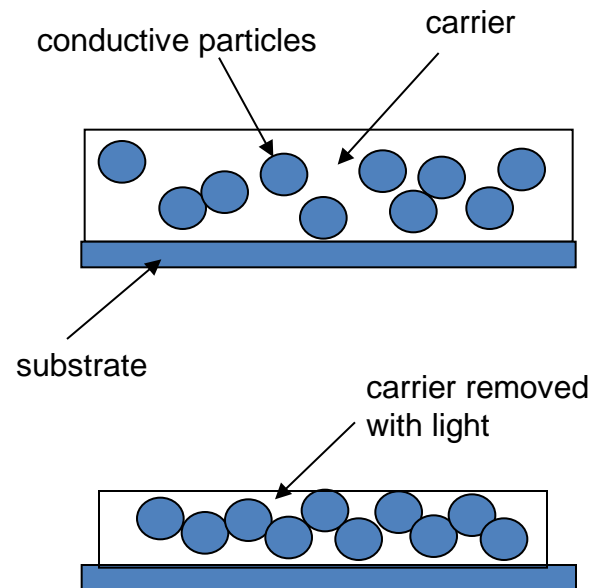
SEM of Silver Nano particle
5-6nm in size



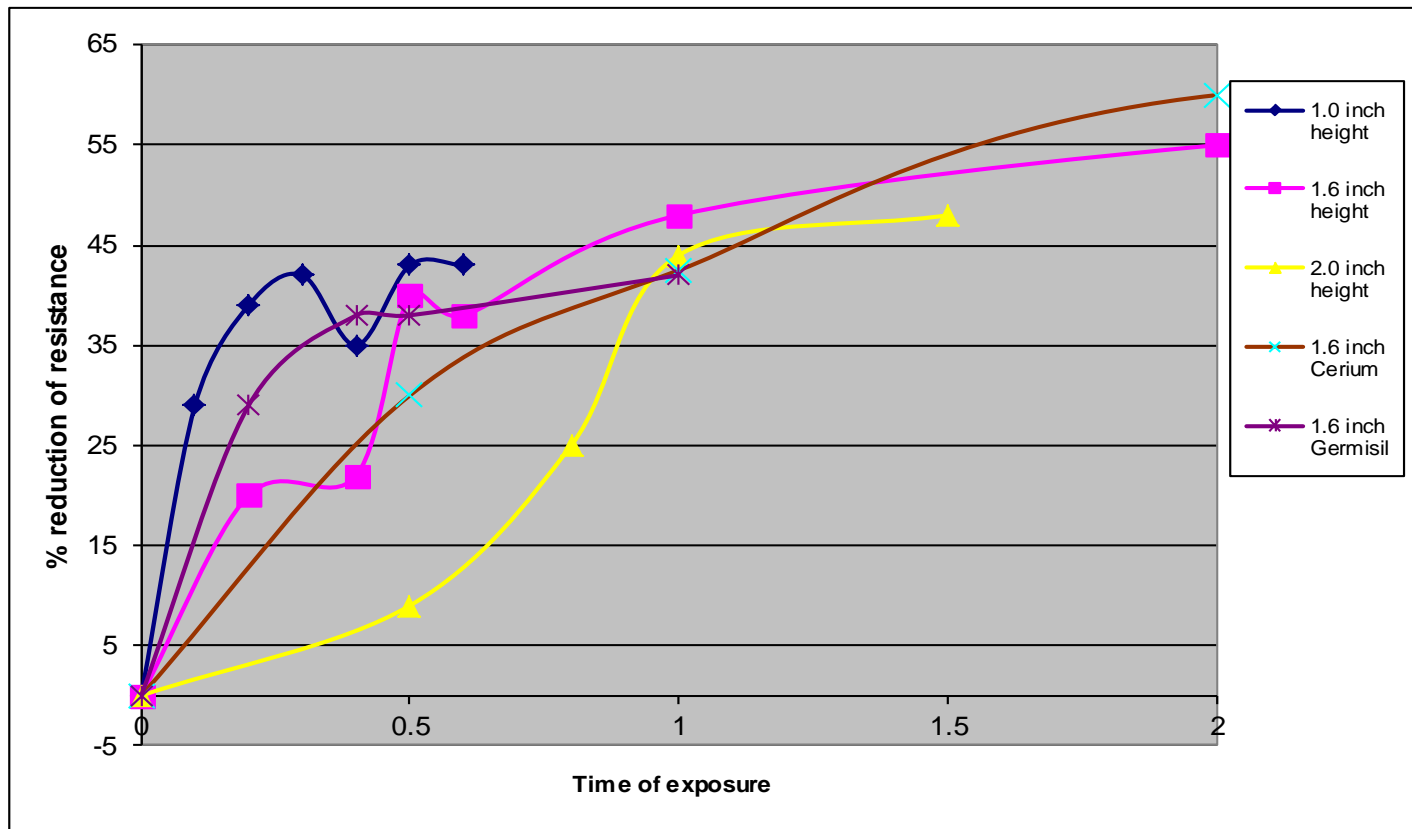
AG Film on PET

Silver Ink Tests

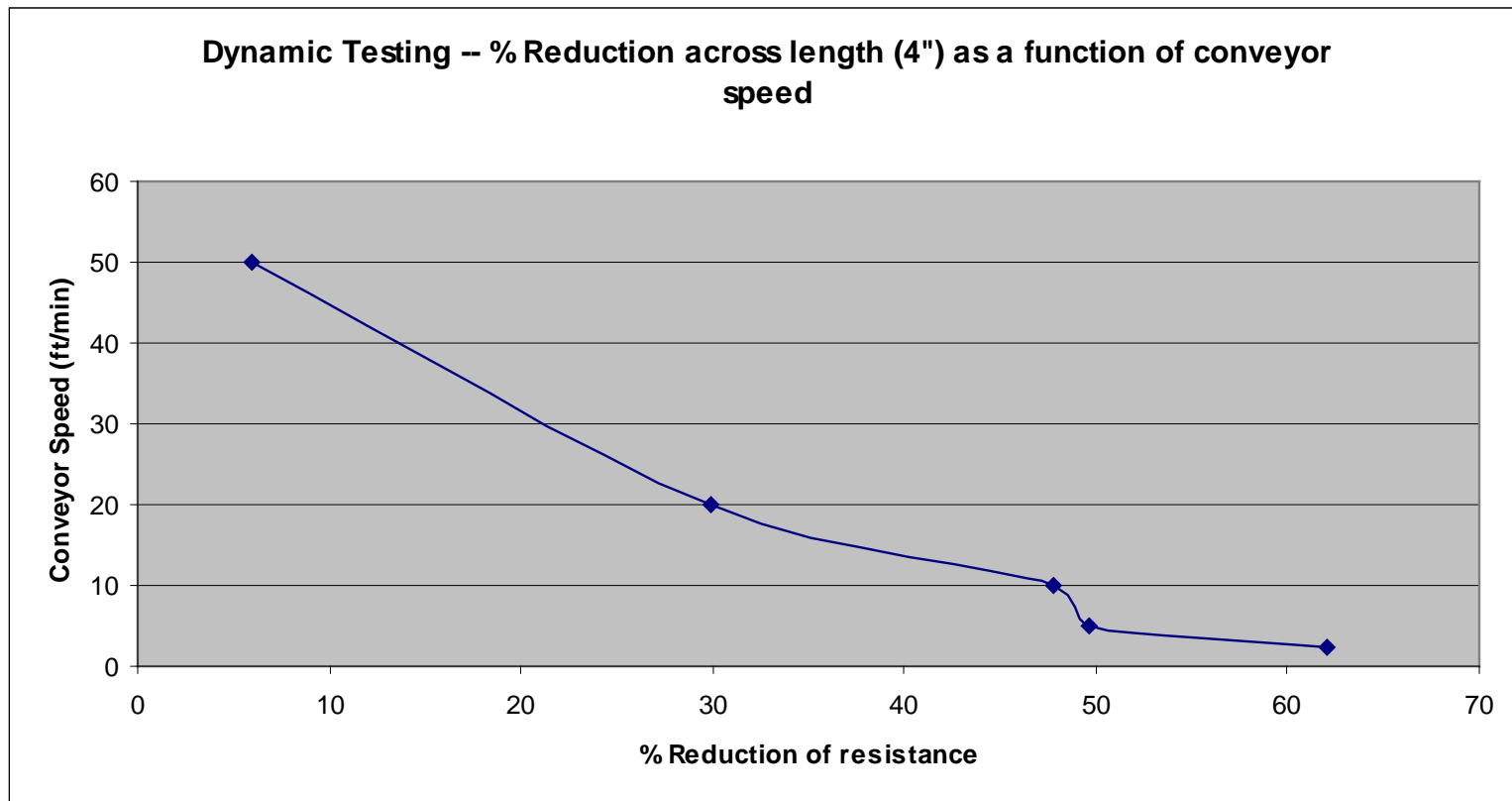
- * We have the greatest success with photonic sintering of silver.
- * Silver requires lower energy per pulse and can be flashed a number of times to bring the resistivity down. This means that stitching problems can be effectively mitigated
- * It seems like total incident energy is the dominant factor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



Silver Test Results

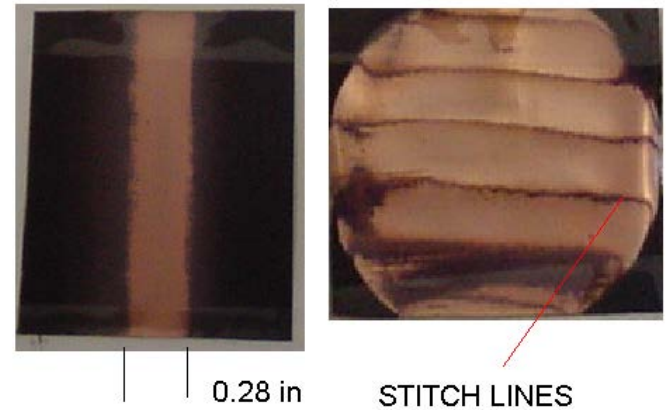


Silver - Dynamic testing



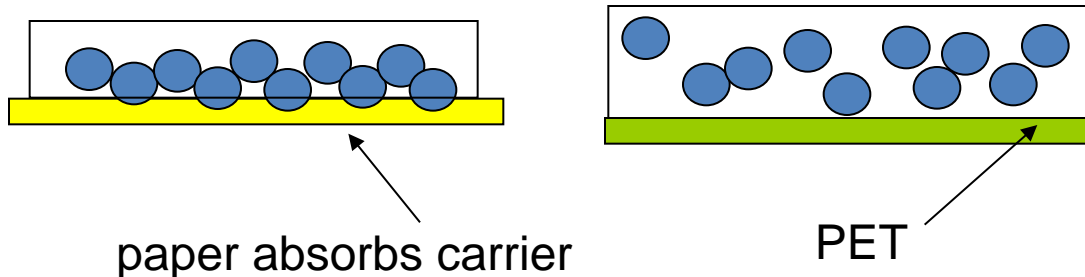
Stitching

- * 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

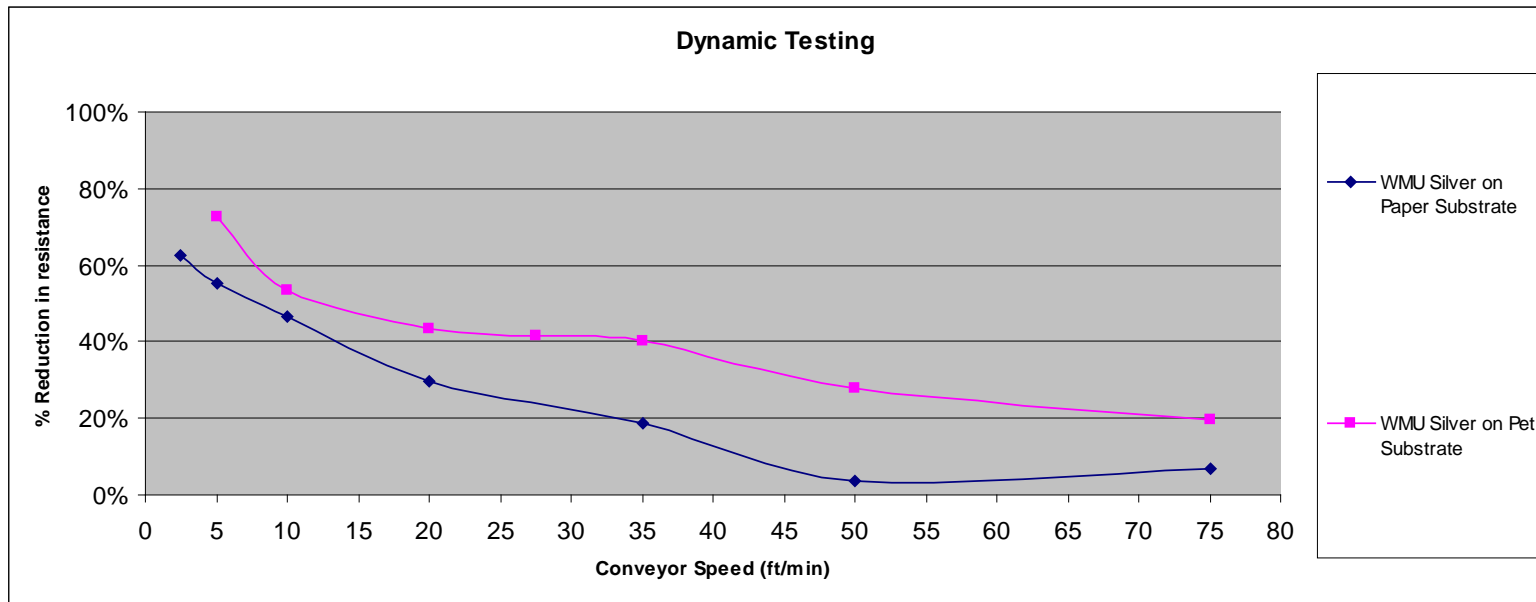


Substrate Types

- * 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.

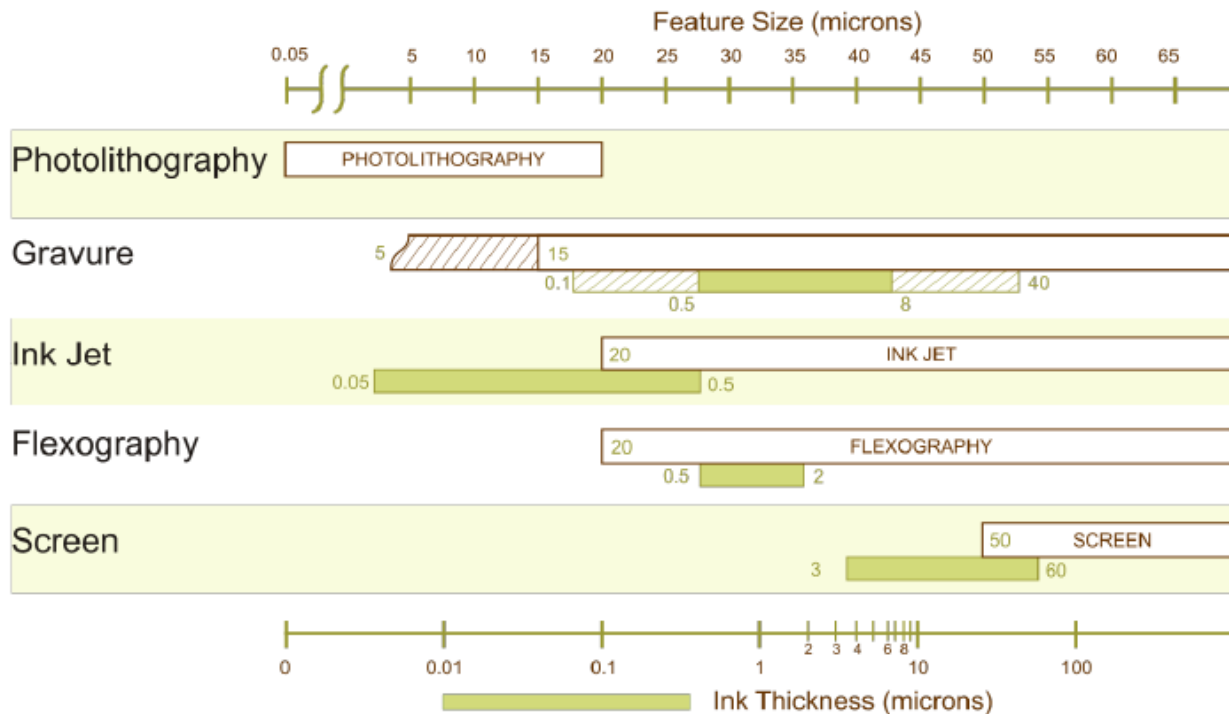


Dynamic testing for different substrates



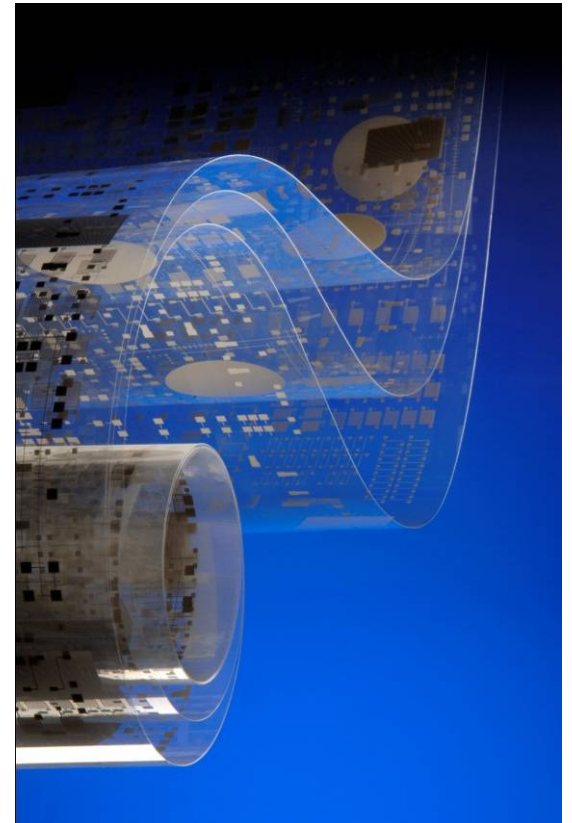
Printing Process

- * 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



Silver- Multi Lamp System Design

	5	10	15	20	25	30	35	40	45	50	55	60
2.5	1	1	1	1	1	1	1	1	1	1	1	1
5	1	1	1	1	1	1	1	1	1	1	1	2
10	1	1	1	1	1	1	1	1	1	2	2	3
15	1	1	1	1	1	1	1	2	2	2	3	5
20	1	1	1	1	1	1	2	2	2	3	4	7
25	1	1	1	1	2	2	2	2	3	3	5	9
30	1	1	1	1	2	2	2	3	3	4	6	10
35	1	1	1	2	2	2	3	3	4	4	7	12
40	1	1	2	2	2	2	3	4	4	5	8	14
45	1	2	2	2	2	3	3	4	5	5	9	15
50	2	2	2	2	2	3	4	4	5	6	10	17
55	2	2	2	2	3	3	4	5	5	7	11	19
60	2	2	2	2	3	3	4	5	6	7	12	20
65	2	2	2	2	3	4	5	5	6	8	13	22
70	2	2	2	3	3	4	5	6	7	8	14	24
75	2	2	2	3	3	4	5	6	7	9	15	25
80	2	2	3	3	3	4	5	7	8	9	16	27
85	2	3	3	3	4	5	6	7	8	10	17	29
90	2	3	3	3	4	5	6	7	9	10	18	30
95	3	3	3	3	4	5	6	8	9	11	19	32
100	3	3	3	3	4	5	7	8	10	12	20	34

Conveyor Speed

Process speeds based on printing technology

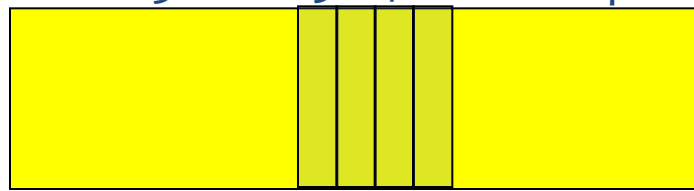
	Basic Principle of Ink Separation on the Image Carrier	Resolution	Ink Film Thickness	Printing Speed
Screen	Ink is pushed through the openings in the imaged mesh	50 μm	3 - 60 μm	8 m/s
Inkjet	Ink droplets are created on demand – no image carrier	20 μm	0.05 – 0.5 μm	2.5 m/s**
Flexography	Topographical – image areas above non-image areas	20 μm	0.5 - 2 μm	5 m/s
Gravure	Topographical– image areas below non-image areas	15 μm	0.5 - 8 μm	15 m/s

Source: WMU CAPE

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

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

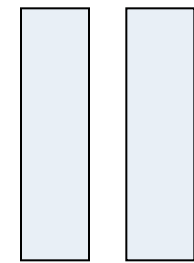


Optical Footprint
Per pulse

Flow Speed



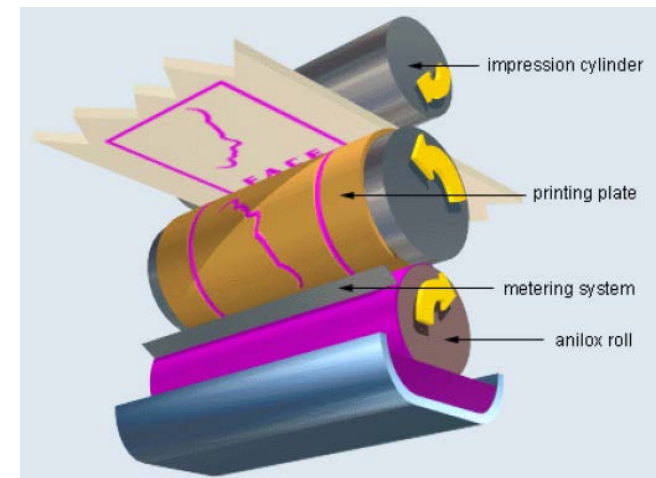
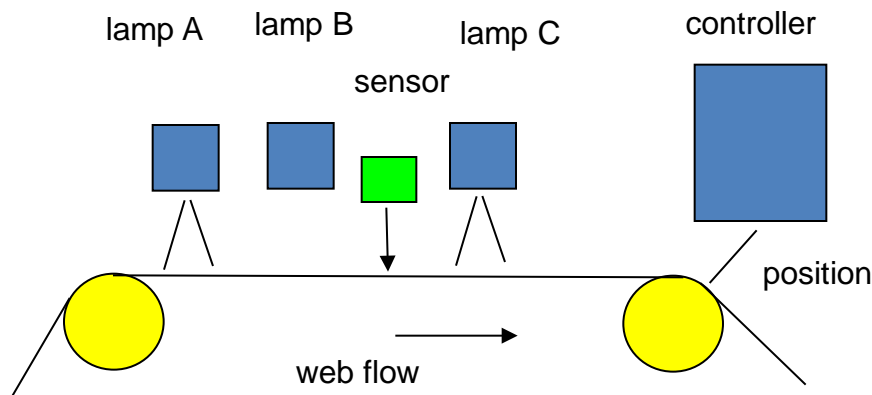
Overlap



Flow too fast for Pulse rate
Banding

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



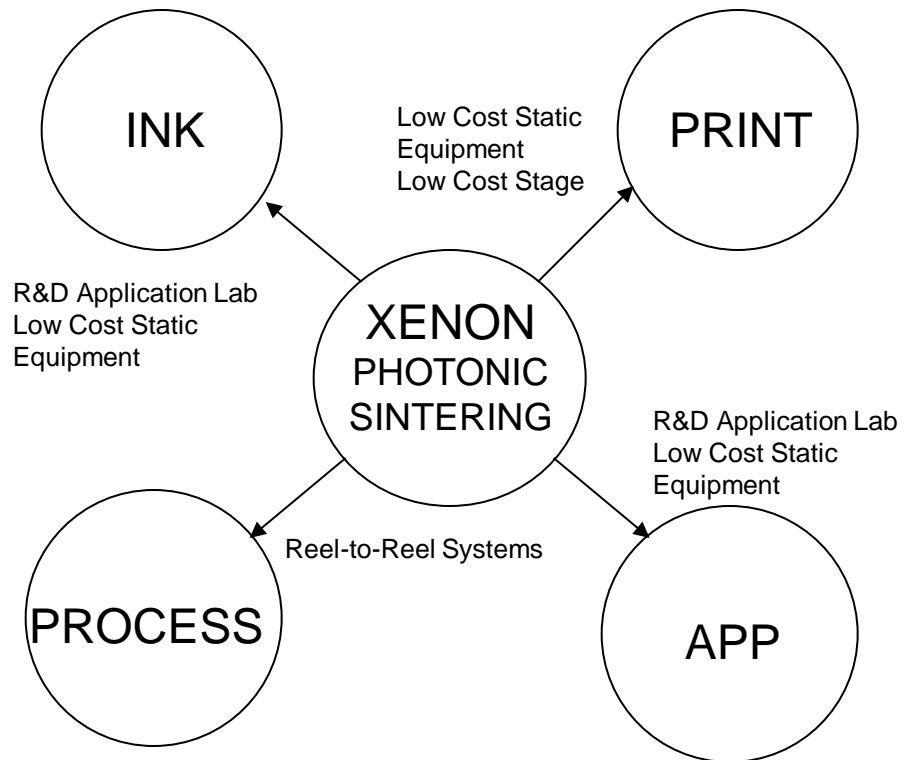
Strategy

Bringing Photonic Sintering to Reel-to-Reel

- * Product development plan
 - * Build flexible low-cost static systems that can establish the key parameters for formulators/manufacturers
 - * Build systems that operate for small-scale, low-speed systems to evaluate stitching
 - * Build multi lamp high speed pilot systems for reel-to-reel developers
 - * Use all of above to provide customized solution for the industry.

Rapid Deployment

- * Success revolves around a program that interacts with all parts of the system
 - * Industry provides application demands that can be tested at Xenon facility
 - * Industry may buy low cost equipment to validate the application
 - * Ink manufacturers can do the same
 - * Print developers can evaluate systems on a small scale with moving stage
 - * These groups can interact to optimize and parameterize the application
 - * Process developers can use all these components to develop custom reel-to-reel systems
- * Must establish symbiotic and synergistic partnerships



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



Partnerships



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

Comments

- * Thanks for inviting me.
- * For further details see us at Booth 1924
- * Contact info:

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- * Questions /Comments