

Broadcast Photonic Curing of Metallic Nanoparticle Films

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ABSTRACT

A novel and industrially scalable technique is presented for curing metal nanoparticle based films in which an uncured film is made conductive by exposure to a brief, intense pulse of light from a xenon flash lamp.

This technology heats and fuses the metal nanoparticles without significantly heating the substrate. Since the technique is broadcast by nature, no critically aligned optics are required. By nature of their high surface to mass ratio, high absorptivity, poor thermal conductivity, and low thermal mass, the nanoparticles are heated by the pulsed light source without significantly heating the substrate or other thermally sensitive components. This allows a complex pattern to be instantly cured even on low temperature substrates.

Data from both silver and copper based films are presented. Sheet resistances as low as $20 \text{ m}\Omega/\square$ and resistivities as low as 4X bulk have been attained with silver. Sheet resistances as low as $150 \text{ m}\Omega/\square$ and resistivities as low as 40X bulk have been attained with copper. Typical substrates are cellulose and PET and typical films are 0.5-5 microns thick.

In addition to silver, this technology enables the printing of copper conductive patterns with high speed printing techniques as the short time of heating fuses the particles before they have the opportunity to significantly oxidize. Thus, no reducing or inert atmosphere is required to cure the film and attain high conductivities.

Keywords: conductive, silver, copper, curing, photonic

1 INTRODUCTION AND MOTIVATION

One of the goals of flexible electronics is the reliable deposition and curing of high-resolution, highly-conductive patterns on low temperature substrates such as paper or plastic. Typically, these substrates are low-cost and unfortunately, thermally fragile. One of the many approaches to making these patterns is to deposit nanometer sized metal particles, usually silver since it is highly conductive and does not oxidize readily. By using nanometer-sized particles, high resolution can be achieved. Typically nanoparticles are synthesized in a wet process, and a capping group is placed on the surface of the particles. This capping group helps prevent them from

aggregating in solution. When the solution is applied to a substrate and dried, it is usually heated to volatilize the capping group and allow the particles to contact and sinter. A further motivation of using nanoparticles is that lower curing temperatures can be realized as they have a depressed sintering temperature. Still, the temperature limitation is often dependant on the thermal decomposition of the substrate.

Cost is one of the drivers for the manufacture of flexible electronics. By being able to process at lower temperatures, cheaper substrates can be used. Since the sintering of particles is a time-temperature process, lower processing temperatures generally mean longer processing times. This is problematic since a cure time of 1 minute on a 2000 fpm web necessitates offline curing or requires a curing oven nearly half a mile long. This suggests a high-temperature short-time approach to curing. If this is done in conjunction with a particle specific heating process, one can solve the somewhat paradoxical problem: heat the particles enough to sinter them but without damaging the underlying substrate.

By reducing the time to cure to less than a millisecond, such a curing process can be compatible with high-speed printing processes such as gravure and flexography without taking up a large amount of floor space or curing offline. In essence, the time to cure becomes matched to the time to print.

2 BASIS OF TECHNOLOGY

2.1 Basic Process

The general motivation for using this process is based on the physical properties of nanoparticles. Metal nanoparticles are generally black and therefore very light absorbing.¹ They have a very high surface area to mass ratio hence very little light is needed to heat the particles. A continuous source of radiation will heat up the particles, but within a few milliseconds they will transfer heat to and attain thermal equilibrium with the substrate. An intense pulse of radiation with a duration shorter than the thermal equilibration time of the particles and the substrate can heat the nanoparticles quickly enough to sinter before they transfer much energy to the substrate. We have experimentally found that the ideal radiant energy is of order 1 J/cm^2 deposited in about 1 ms for most systems of

interest. Longer pulses require more energy to cure the particles and transfer too much heat to the substrate. Shorter pulses can vaporize smaller particles in the film, build up thermal gradients in the substrate, and explosively blow apart the film by doing PdV work on heated voids in the film. The particle type, size, film thickness, substrate type, substrate thickness, and particle binder system all play a role in determining the ideal curing conditions.

For a printed pattern on a low temperature substrate, this is an ideal curing technology. Since the particles are preferentially heated, broadcast curing heats only the deposited pattern. The substrate and surrounding components are kept cool. A corollary to this is that multiple layers can be built up and cured without placing a thermal load on previously cured layers.

Since the particles are very absorptive, this technique is limited to thin films. We regularly cure films from 0.5-5 microns thick. This is the thickness range typical of the high speed printing industry.

2.2 Why not lasers?

A xenon strobe is used for this process. A laser may appear to be the most logical choice. However, the unique qualities offered by a laser such as coherence, narrow wavelength range, and ability to focus to small spot size are not needed for this application. A laser is a very expensive source of light as the hardware is complex. The electrical to light conversion efficiency of a xenon strobe (~50%) is greater than 10 times than that of the type of laser needed to cure metal particle based films. Since this process is a broadcast curing technique, critical and expensive alignment of a laser-based optical system is not needed since the nanoparticles are preferentially heated leaving the rest of the substrate cool. For a given throughput, a laser-based system is an order of magnitude more expensive than the system being pursued. For low throughput, small spot curing, a pulsed, solid-state laser could be more desirable, but not necessarily, as a strobe is often used to pump a laser.

3 BASIC PLATFORM

3.1 Hardware Development Background

This high-speed process for curing metal nanoparticle films has its origin in Nanotechnologies' nanoparticle synthesis process.² This process begins with two metal rods in an enclosed tank. A high-power (50-100 kA), pulsed (~1 ms) arc discharge is drawn between the rods in an atmospheric pressure gas. The material at the end of the rods is ablated and heated to form a high-pressure (10-100 Atm) metal plasma. The plasma supersonically expands into the surrounding gaseous atmosphere, which quenches the plasma at approximately 1,000,000 K per second yielding nanometer sized, single crystal, unaggregated particles in a gas suspension. These particles are conveyed

out, collected, the rods are indexed in toward each other, and the process is repeated at several times per second to make up to several kg of material per hour. By changing the composition of the quench gas from inert to reactive, either metals or metal compounds can be made. A TEM of 25 nm nanosilver (average particle size via BET method) made with this process is shown in Figure 1. This material is synthesized with a trace amount of carbon to prevent the particles from aggregating. It is easily removed with a variety of techniques.³

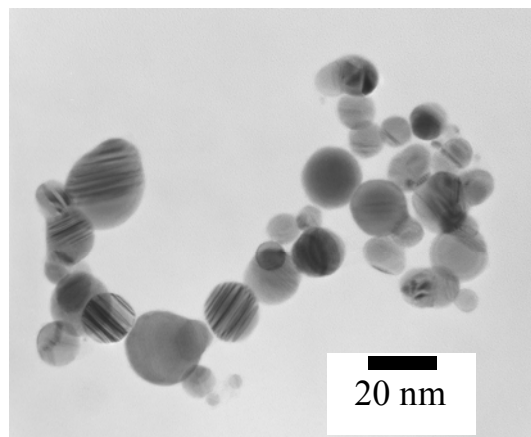


Figure 1: TEM of 25 nm silver made with Nanotechnologies' pulsed plasma process.

A similar process is used to generate the intense light needed to photonicly cure nanometal-based films. Here, the typical arc discharge current has been lowered to below the threshold that would ordinarily ablate the electrodes and make nanoparticles. This is about 10 kA, but the radiation is still dramatically more intense than that from a typical camera strobe. Similar to the nanoparticle synthesis process, both the pulse duration and the intensity can be varied. This give independent control over both the power and energy delivered to a surface.

3.2 Research and Development System

A research and development system was built to scan curing conditions to optimize the conductivity of several films and substrates. The cure area, areal energy density, and the pulse length of the arc discharge are all adjustable. The R&D system is shown in Figure 2. It was used to process all of the films referred to in this paper. Its abbreviated specifications are:

- Adjustable strobe energy (10 to 1000 Joules)
- Adjustable strobe pulse duration (20 to 500 μ s)
- 30 cm (12") wide x 1 - 3 cm cure pattern
- Strobe height above sample adjustable from 0.5 cm to 8 cm
- Strobe rate adjustable from single pulse to 2 Hz

- Enclosed and interlocked strobe region for personnel safety
- 3 kW strobe power supply (220VAC 3-phase, 30 Amp power required)



Figure 2: R&D photonic curing system.

4 PERFORMANCE DATA AND RESULTS

Typical energies required to cure films are 0.5-2 J/cm². This is comparable to the amount of energy required to heat up a 1-micron thick layer of silver from room temperature to its melting point.

The silver and copper nanoparticles were synthesized by Nanotechnologies and were dispersed on site. The wet films were typically applied to the substrates with a wire wound rod.

Table 1 shows photonic cure data for silver on Mylar. Initially, the conductivity is barely measurable, even with a 2-point probe before the film is cured. All resistivity data is derived from a 4-point probe. Figure 3 is a graph of Table 1 in the cure range of interest. In general, increasing the areal energy density increases the conductivity of the film. At some point, the power deposited becomes too high and the film begins to lose its integrity. In this specific case, a better cure can be achieved with less energy using a 100 μs exposure versus a 300 μs exposure. A 30 μs exposure produces less well behaved, although quite repeatable, results. The specific mechanisms are still under investigation.

The best repeatable data achieved to date for a silver ink we developed attains about 15X bulk silver resistivity with a room temperature cure on paper. Photonic curing

brings down the resistivity to about 4X bulk with a sheet resistance of 20 mΩ/□.

Pulse Length	Areal Energy Density J/cm ²	ρ (micro-ohm cm)
300 μs	0.38	1228535
	0.63	2443
	0.86	97
	1.03	63
	1.12	51
	1.22	49
100 μs	1.42	56
	0.31	592345
	0.49	254
	0.70	87
	0.90	61
	1.13	49
30 μs	1.38	64
	1.65	133
	0.39	4793
	0.54	293
	0.70	144
	0.88	155
	1.05	128
	1.32	90
1.42	70	

Table 1: Photonic cure resistivity data for a 2.5 micron thick silver film.

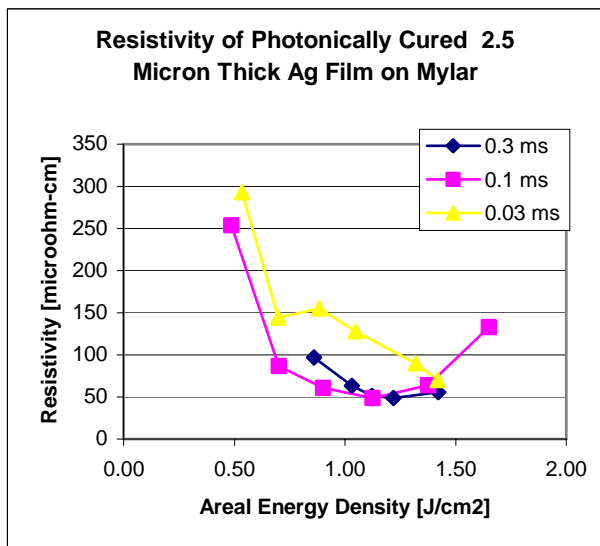


Figure 3: Graph of Table 1 selection showing and optimized cure routine for silver film on Mylar.

Table 2 and Figure 4 show copper cure data. It is notable that copper particle films cannot generally be cured in an oven unless the environment is either reducing or completely inert. All of our films were cured in air. This is possible because the copper particles are heated up so rapidly that they don't have time to oxidize. We have achieved 40X bulk copper resistivity on Mylar with a sheet resistance of about 150 mΩ/□. Continued improvement is

likely as we have made fragile films with resistivity as good as 11X bulk.

Pulse Length	Areal Energy Density J/cm ²	ρ (micro-ohm cm)
300 μ s	0.75	140
	0.78	100
	0.81	100
	0.84	86
	0.86	80
	0.88	79
100 μ s	0.34	387
	0.41	198
	0.49	123
	0.57	96
	0.66	83
	0.75	86
30 μ s	0.70	91
	0.73	86
	0.77	72
	0.81	82
	0.83	74
	0.86	75
	0.90	127

Table 2: Photonic cure resistivity data for a 2.5 micron thick silver film.

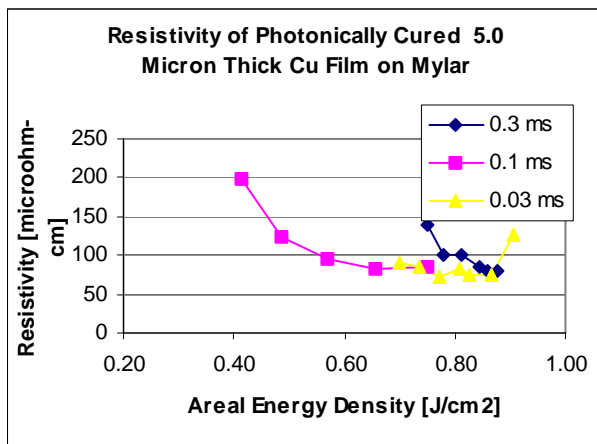


Figure 4: Graph of Table 2 selection showing and optimized cure routine for copper film on Mylar.

We have cured silver and copper films on a variety of low and high temperature substrates including PET, various types of paper, polycarbonate, Kapton, silicon, glass, FR-4, acetate, polyethylene, and polystyrene.

We have incorporated binders and adhesion promoters into some of our films. A binder can interfere with electronic conduction, but it allows a higher intensity cure, so the ultimate conductivity realized can be higher than a pure particle system.

Metal nanoparticles are easiest to cure, but we have scanned our system with particles nonideal to the process such as micron sized metal particles or even nonmetallic particles with success. It is notable that we have made

previously cured commercial inks more conductive with this technique with no detectable degradation of the film or substrate. We are pursuing other applications.

5 COMMERCIAL SYSTEM

A commercial photonic curing system based on the same technology as the R&D system is currently under development. This system will be able to economically process a continuous product stream with high throughput at rates up to 50 ft/min in a reel-to-reel system. Processing cost is projected to be roughly \$0.01 per square foot (\$0.11 per square meter). A schematic of the system is shown in Figure 3.

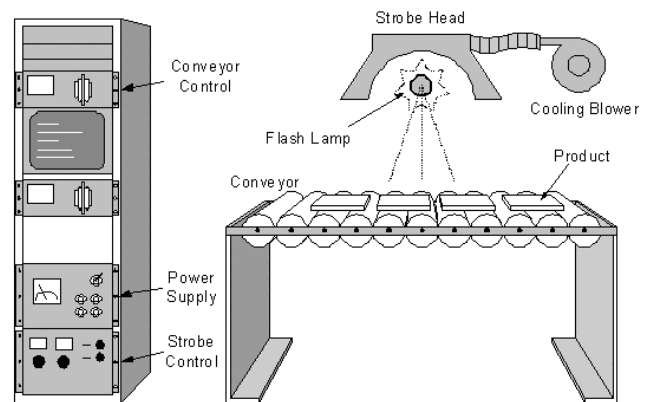


Figure 5: Commercial photonic curing system schematic.

6 CONCLUSIONS

We have demonstrated the broadcast curing of nanometal particle films on low temperature substrates by exposing them to the pulsed emission from a xenon arc discharge lamp. Metallic conductivity is attained without damaging the substrate. An R&D system was built to scan the parameters of the process to optimize the curing for multiple films and substrates. We recently finished a narrow web system that cures metal films at up to 50 fpm on polyethylene and are currently building a wider web, higher speed curing system. We believe this technology is scalable to match high speed printing processes and may have applications beyond conductive patterning.

REFERENCES

- [1] Yang, Y. et. al., "Propagation of Shock-induced Chemistry in Nanoenergetic Materials: the First Micrometer," *Journal of Applied Physics*, **95**, 7, p. 3667, (2004).
- [2] US Pat. #6,777,639.
- [3] Caudillo, R. et. al., "Ferromagnetic Behavior of Carbon Nanospheres Encapsulating Silver Nanoparticles," To be published in *Phys. Rev. B*.