

# Mechanisms of Photonic Curing™: Processing High Temperature Films on Low Temperature Substrates

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## ABSTRACT

Photonic Curing uses flashlamps to thermally process a thin film at high temperature on a low temperature substrate without damaging it. This has utility in printed electronics, where high temperature curing is generally equated to electronic performance and high speed processing is equated to low cost. Three significant processing advantages are realized over previous technologies:

1. Inexpensive (and flexible) polymer substrates can now be used in place of expensive, rigid substrates while achieving similar performance.
2. Thin films can be cured quickly enough to keep up with high speed printing processes in a small footprint, thus making it suitable for in-line placement with existing print systems.
3. The transient nature of the process has enabled the creation of new types of films on low temperature substrates, including those created by the photonic modulation of high temperature chemical reactions.

In this paper we discuss the mechanisms of the process and model it using a thermal diffusion simulation. The simulation has been integrated into a 4<sup>th</sup> generation high-speed processing tool yielding predictive results.

**Keywords:** photonic, curing, sintering, copper, conductive

## 1 INTRODUCTION

Photonic Curing was introduced by the author at the NSTI conference in 2006<sup>1</sup>. Additional work has been done to model the process including both the radiation absorption and sintering of a silver nanoparticle film<sup>2</sup>. Photonic curing is the use of a flashlamp to transiently heat a thin film to high temperature on a low temperature substrate without damage.

Figure 1. illustrates the main effect we exploit. A high power, short pulse of light is used to heat a thin film of material, such as printed silver or copper nanoparticles, to a very high temperature for a brief amount of time on a low temperature substrate, such as polyethylene terephthalate (PET)<sup>3</sup>. Normally, PET has a maximum working temperature of 150 C. With this technology, we can process a thin film beyond 1000 C on the surface of a PET substrate without damaging it, provided we heat the thin

film up and cool it down very quickly. This is an adequate temperature to sinter many materials including silver and copper. The pulse of light is so fast that the back side of the substrate is not heated appreciably during the pulse. After the pulse is over, the thermal mass of the substrate rapidly cools the film via conduction. The pulse is usually less than a millisecond in duration, and the time spent at elevated temperature is only a few milliseconds. Although the substrate at the interface with the thin film reaches a temperature far beyond its maximum working temperature, there is not enough time for its properties to be significantly changed. This effect is highly desirable as the thin film has now been processed at a temperature not possible with an ordinary oven. It often allows the substitution of low temperature (e.g. cheaper) substrates for higher temperature ones. Since most thermal processes are Arrhenius in nature, i.e., the curing rate is related to the exponential of the temperature, this short process can, in many cases, replace a 150 C oven cure taking minutes! This further means that if the light is pulsed rapidly and synchronized to a moving web, it can replace a large festooning oven in a space of only a few feet. In addition to curing materials quickly, higher temperature materials such as semiconductors or ceramics that can't ordinarily be cured on a low temperature substrate can now be cured using this technology.

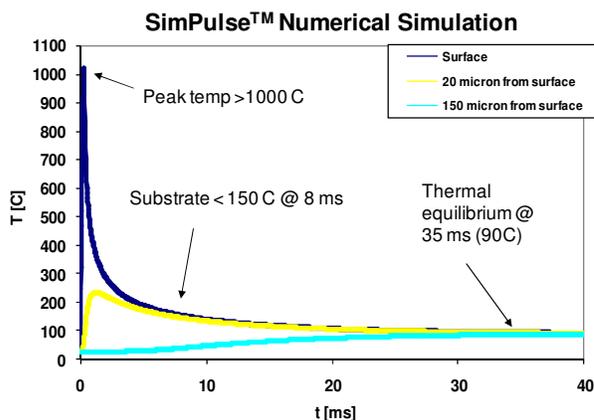


Figure 1. Thermal simulation of photonic curing process (300  $\mu$ s, 1 J/cm<sup>2</sup>) for a 1 micron thick silver film on 150 micron thick PET. Temperatures beyond 1000 C can be achieved on PET without damage.

One of the more remarkable aspects of this technology is that materials can be cured with the economics and uniformity of oven curing but also with the control of laser processing. Photonic curing is completely maskless. Printed thin film traces are heated while the surrounding substrate is not. This can happen because most inexpensive substrate materials, such as PET, PE, PEN, PC, PI or even paper, do not readily absorb light, or more specifically, the absorption depth for most of the emission from our system is a lot larger than many of the materials suitable for films. Thus, they don't get as hot as the thin film does. This effect allows one to cure a printed thin film with pulsed radiation on a low temperature substrate without registration. Of course, the substrate underneath the film does get hot. It gets much hotter than its maximum working temperature, but it does not become damaged. We address that below.

## 2 PROCESS

The basic mechanism of photonic curing is illustrated in Figures 2 and 3. A film of thickness  $x_f$  with thermal equilibration time  $\tau_f$  sits on a substrate with thickness  $x_s$  and thermal equilibration time  $\tau_s$  (Figure 2). Each material has its own thermal coefficients  $c$ ,  $\rho$ , and  $\kappa$ . Here

$$\tau_i = c_i \rho_i x_i^2 / 4 \kappa_i \quad (1)$$

A short pulse of intense light with duration  $t_p$  heats the thin film to temperature  $T_{peak}$ .  $T_{peak}$  is typically far beyond the maximum working temperature of the substrate  $T_{max}$ . The film is rapidly cooled via conduction to the substrate (Figure 3). The side of the substrate adjacent to the film, which is usually a polymer, is at an elevated temperature, usually far beyond its published maximum working temperature, for such a short period of time that the polymer does not have time to unwind and significantly change its properties.

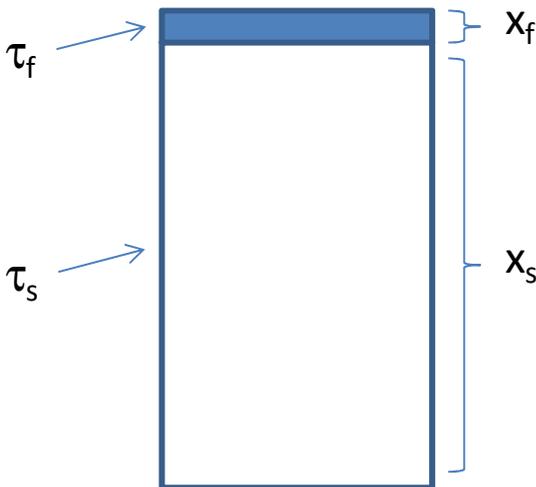


Figure 2. Typical thin film stack.

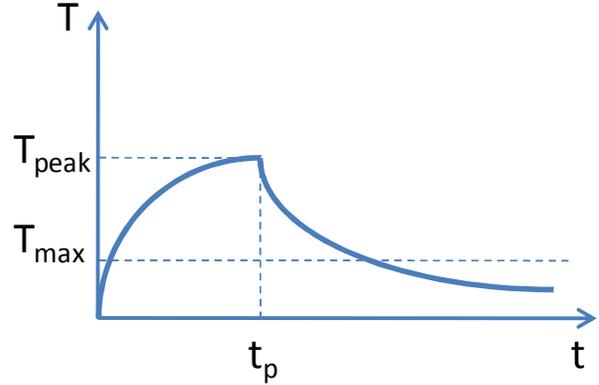


Figure 3. Transient surface heating and subsequent relaxation of a thin film on a comparatively thick substrate.

### 2.1 Transient Curing Conditions

We have established three transient curing conditions for optimal high temperature processing of a thin film on a low temperature substrate:

$$x_f \ll x_s \quad (2)$$

$$t_p \ll \tau_s \quad (3)$$

$$\tau_f \ll t_p \quad (4)$$

In the example shown in Figure 1,  $x_f = 1 \mu$  and  $x_s = 150 \mu$ .  $\tau_f$ ,  $t_p$ , are  $\tau_s$  are  $1.9 \times 10^{-10}$  s,  $3.0 \times 10^{-4}$  s, and  $2.3 \times 10^{-2}$  s, respectively. Thus, the transient curing conditions are readily met. When this is the case, the thin film can be heated to near the gasification temperature of the substrate without significant permanent damage. These transient curing conditions warrant further discussion.

- (2) The thickness of the film needs be much thinner than the thickness of the substrate since we rely upon the thermal mass of the substrate to cool the thin film via conduction. If the thin film is not cooled down quickly enough, such as when the substrate thickness is of order the thin film thickness, the processing temperature that can be reached without damage to the substrate is much lower.
- (3) The second condition insures the heating is complete long before the energy has the opportunity to heat up the bulk of the substrate which would reduce the thermal gradient in the substrate and reduces the cooling after heating.
- (4) Since a minimum amount of energy is needed to process the thin film, an increasingly short pulse length dictates an increasingly high power. This

condition is almost always met if the film were fully dense. However, a *printed* film, has porosity, left over solvents, and binders. When it is heated by pulsed radiation, the effective  $\tau_f$  is several orders of magnitude longer than that calculated by (1) since the volatiles must be boiled off before it can reach a high processing temperature.

When  $\tau_f$  is very short, changes to the thermal conductivity,  $\kappa_f$ , of the film, is do not significantly affect the process conditions. Conversely,  $\kappa_s$ , the thermal conductivity of the substrate, plays an integral role in the process. When the transient curing conditions are satisfied, the radiant power needed, assuming constant power input, the peak temperature reached in the film,  $T_{max}$  is:

$$P \sim \sqrt{\kappa_s} \quad (5)$$

Thus, curing a thin film on glass, which has about 6 times the thermal conductivity of PET requires about 2.5 times more power. A silicon substrate requires about 25 times more power than PET. Additionally, lower temperature materials, such as polymers, tend to have a low thermal conductivity. It is not only much easier to create a thermal gradient in a low temperature material, but Photonic Curing generally isn't necessary when thermally processing on high temperature substrates such as silicon as they can withstand high temperatures in equilibrium. This is why we refer to Photonic Curing as "High temperature processing on low temperature materials<sup>TM</sup>".

## 2.2 Process Limitations

There is a minimum amount of energy needed to practically process a thin film at a given temperature. When too much energy is used, the substrate permanently warps. This is analogous to using too high of a temperature in an oven. The main difference is that the oven is an equilibrium heating process and the warping happens during heating. In contrast, the warping happens *after* heating with this process. Consequently, external convective or conductive means during and after processing can help alleviate this type of failure mode.

As the processing time is reduced, the amount of energy needed is less. However, arbitrarily reducing the processing speed means that the processing temperature must be subsequently increased. When the temperature of the thin film exceeds the gassification temperature of the substrate, the film is lifted off resulting in a clean ablation. This is the first type of film failure caused by the application of too much radiant power.

Another type of failure due to too much power is caused by internal gas generation within the film.. If the film is too porous, has too much solvent in it, or has volatile binders, the application of too much radiant power will result in a cohesive failure of the film. This can be

remedied by predrying with lower power pulses of light or lowering the power and increasing the pulse length of the processing so as to avoid this type of failure.

These process limitations are shown in Table 1.

Limitation type	Processing limit	Symptom
Energy	Substrate heated beyond maximum working temperature after thermal equilibrium	Substrate warping
Power	Maximum temperature reached is greater than the gasification temperature of the substrate	Clean film ablation
Power	Gas generation within the film	Cohesive failure of the film

Table 1. Processing limitations and symptoms for transient thermal processing of a thin film on a low temperature substrate.

## 3 SYSTEM

Early on, we chose to use flashlamps for our pulsed radiation source. They are an excellent source of light for many reasons. When Xenon is used as the fill gas, they have about a 50% quantum efficiency. In a well designed system, approximately 30% of the electrical input energy goes into light. This is an order of magnitude more efficient than a good laser and it does so without complex optics. The emission is generally more flexible than a laser for many curing applications as some portion of its broadband emission (uv to near IR) is absorbed by most thin films we wish to cure. Since the quantum efficiency is so high, undesirable wavelength bands can be filtered out with plenty of light to spare. Additionally, the large beam size 100-1000 cm<sup>2</sup> means that the uniformity of cure can rival that of an oven.



Figure 4. PulseForge® 3300 Photonic Curing™ system.

Our first lab system had only a few fixed pulse lengths. This was found to give interesting results, but control similar to a laser was needed for high fidelity processing. Our current system called PulseForge® (Figure 4), uses Pulse Width Modulation, so any pulse length and shape can be created. This is needed to tailor the temperature profile within a thin film stack for optimal processing. We have written a thermal stack simulator, called Simpulse™, and integrated it into the tool to predict the thermal profile of a thin film stack as a function of the 10 continuously adjustable process variables. This makes it suitable for sintering or annealing many types of materials including metals, semiconductors, and even ceramics – all on low temperature substrates. We have measured delivered peak radiant power greater than  $70 \text{ kW/cm}^2$  in the laboratory with the PulseForge model 3300, but  $\sim 30 \text{ kW/cm}^2$  is the recommended industrial operating limit. Pulse lengths are as short as  $30 \mu\text{s}$ . Combined with a moving web, a custom time-temperature profile can be created in a thin-film stack for an arbitrarily long length of cure. Because the system is electronically controllable, means for Closed Loop Process Control (CLPC) is inherent to the system. The flashlamps and electronics are all water cooled, so the system can cure material at industrial speeds ( $>100 \text{ m/min}$ ) in a wide web format.

## 4 CONCLUSIONS

We have established three transient curing conditions for optimal high temperature processing of a thin film on a low temperature substrate using photonic curing. A high-speed commercial photonic curing system with 10 process variables has been developed to exploit this effect. The system contains an integrated thin film stack thermal simulator with predictive capability. We have also identified three process limitations which serve as a guide for optimization of the process.

## REFERENCES

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