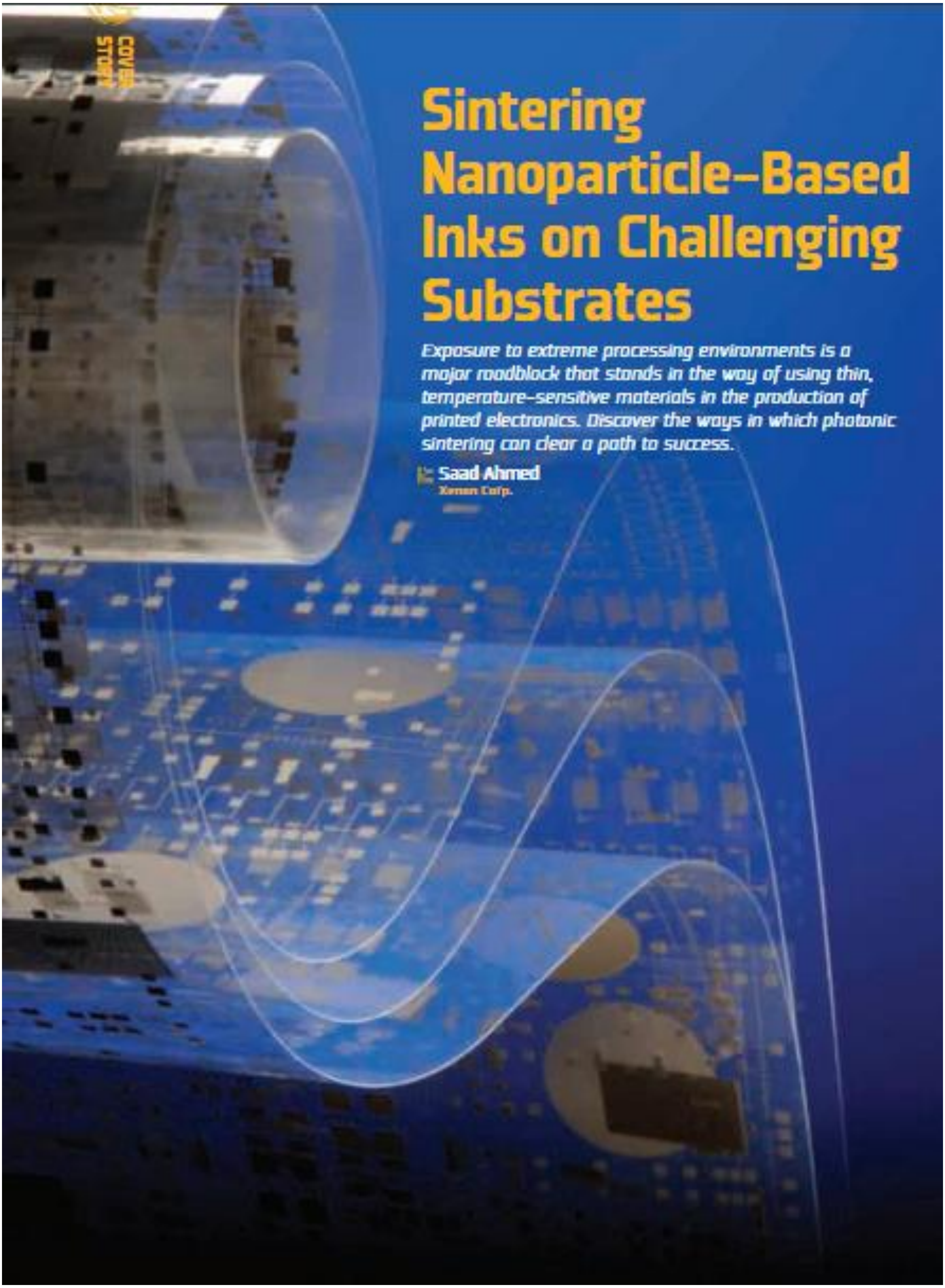

Sintering Nanoparticle-Based Inks on Challenging Substrates

Exposure to extreme processing environments is a major roadblock that stands in the way of using thin, temperature-sensitive materials in the production of printed electronics. Discover the ways in which photonic sintering can clear a path to success.

Saad Ahmed
Xenon Corp.

We live in a world surrounded by electronics. Even though the technology for manufacturing devices and components has advanced in leaps and bounds, the basic printed circuit board (PCB) has not changed significantly. The process of applying photo resist to a sheet of copper that is fixed on a rigid board and using a photo-lithographic process with a chemical-etch process to create tracks and pads to form interconnects between components is still the most common way of building PCBs.

Conventional PCB creation is a subtractive, multistep process that requires chemicals, is wasteful of copper, and does not lend itself to a high-speed, low-cost solution. In some special cases, flexible or rigid-flex PCBs are used, but they are based on the same principles of standard PCB manufacture but use flexible plastic substrates instead of rigid materials.

An alternative approach to PCB manufacture is to print the copper traces on the substrate rather than etch away unused copper ***(Figure 1)***. This would be a totally additive process and would eliminate the need for lithography and etching. High-speed printing processes could then be used to mass produce circuit boards at a very low cost. Low-cost substrates such as paper or PET could be used to produce circuits that are cheap enough to be disposable; however, we must overcome some significant challenges to achieve that goal.

The most important challenge is that of resistivity. Copper, silver, and gold, which are often used in PCBs, are very good conductors and have very low resistivity. This property allows circuits to run more efficiently. Conduction though metals is possible because electrons are free to move about the metal lattice. Resistance increases when metal clusters are deposited in ink form because the lattice is disjointed. Gaps and voids between metal particles do not allow for the free movement of electrons, which causes increased resistance. Ideally, the metal particles would be melted together or sintered to form a homogenous strip of metal to achieve the resistivity. However, melting points of metals are typically very high. Gold, as an example, melts at 1064°C, and this amount of heat means that low-temperature substrates, such as paper and PET, are not useable. But all of this has changed with the advent of nanoparticle-based inks.

SINTERING NANOPARTICLE-BASED INKS

Nanoparticles are defined as particles as small as 1-1000 nm. In general, particle sizes up to 100 nm most commonly fit the description. A particle's physical characteristics change as it becomes smaller, including absorption characteristics and melting point ***(Figure 2)***. Melting-point depression is a phenomenon expressed by metal nanoparticles. In normal scales, the melting point of the material does not depend on site. As particles become smaller, their surface-area-to-volume ratio changes such that the atoms on the outer surface become more loosely attached, which causes the melting point to decrease. Lowering the melting point allows the use of a low-bake oven – a system that maintains a temperature below 200°C-for sintering nano-inks without damaging the substrate. The time required for this process is approximately 10 minutes and, therefore, makes high-speed roll-to-roll processing difficult.

Nanoparticles absorb light ***(Figure 3)*** and react by heating up. Melting-point depression and light absorption allow nanoparticles to be sintered effectively with high-energy light sources such as lasers or flash lamps. Using flash lamps is simpler, particularly when large-area processing is required. In addition, the use of a broadband source, such as a xenon flash lamp, is more effective for inks that have a spread of particle size and a wide absorption region.

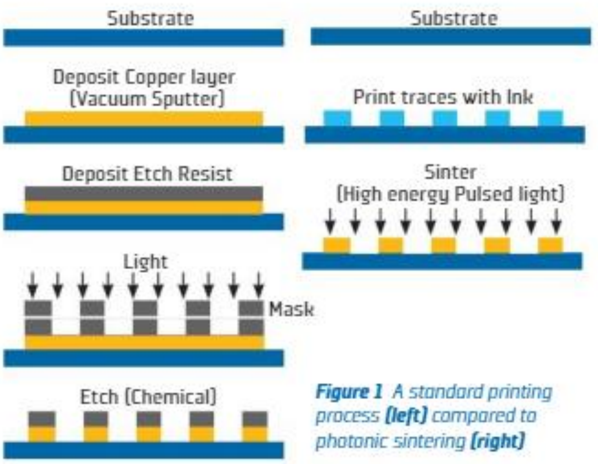

Figure 1 *A standard printing process **(left)** compared to photonic sintering **(right)***

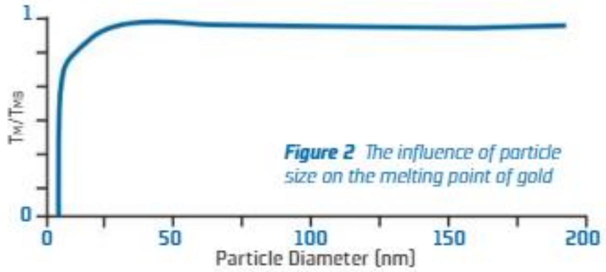

Figure 2 *The influence of particle size on the melting point of gold*

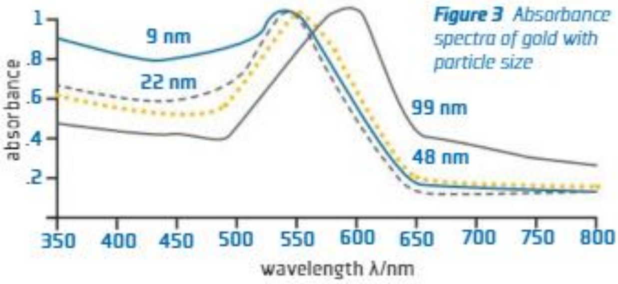

Figure 3 *Absorbance spectra of gold with particle size*

Nanoparticles lose their properties once they are sintered, and they behave similar to bulk materials. The process is, therefore, self-limiting in that multiple flashing does not improve the resistivity significantly and limited sintering takes place. This behaviour raises an important challenge in the use of pulsed light for sintering related to stitching. All light sources have a limited exposure area. The boundary between the exposed area and unexposed area creates partial sintered regions. The overlap region is defined as the stitch when two adjacent boundaries are flashed. These partially sintered regions, when flashed again, behave differently from the fully exposed areas. This change is observable as differences in resistivity across the stitch region. Careful control of the boundary profile, light energy, and overlap can reduce the effect of stitching significantly. However, the most significant factor is the nano-ink formulation used. Inks designed for multiple flashing generally mitigate the effects of stitching.

Resistivity of sintered inks is generally higher than that of bulk material because of the final material's remaining porosity after sintering. Resistivity values of four to five times that of bulk is considered a good result. Some self-drying inks can achieve resistances of six times bulk. Photonic sintering to date has achieved results ranging between three and five times bulk for certain inks.

Ink formulation plays a major role in photonic sintering. The ink-deposition method must be suited to the ink in terms of viscosity and surface tension. The formulation also determines the drying time for the inks and the adhesion of the ink to the substrate. Photonic sintering performs better with dry ink because pockets of solvent that are trapped in the ink are likely to expand and erupt when exposed to a high-energy light pulse. This causes inks to blow off of the surface, which leads to a reduction in resistivity.

SUBSTRATES

Substrate selection is another important factor. Interestingly, paper and specially coated paper are very good substrates because they can absorb the ink and wick away the carrier agents in the ink. This allows the ink to dry effectively and improves ink adhesion. PET and Teflon are also good substrates to use because they are good insulators and, therefore, allow more photonic energy to be absorbed by the ink rather than the substrate. These substrates are often transparent, which means they absorb less light and, in doing so, allow for greater amounts of pulsed-light energy in the sintering process.

Print-related anomalies are less tolerable when dealing with functional inks. Errors in printing can lead to short and open circuits and, if critically located, can render the printed electronic circuit unusable. Ink-layer thickness, which affects resistivity, also becomes more critical.

Most PCBs are based on two or more layers of conductive traces with vias between them. As circuits become more complex, the trace width, gap between traces, and via sizes are made smaller. High-precision printing is required to overcome the challenge. However, multilayer printing on flexible substrates brings an additional problem to the forefront; substrate expansion. When PET is used in a roll-to-roll application and is drawn through the printing process, the material is under tension, which causes elastic deformation. Heating the material can increase this single-axis deformation. Failure to account for this deformation leads to mismatched layers and a loss of connectivity.

Placement of ICs and other components is another consideration when working with low-temperature, flexible surfaces. Soldering, which is the traditional method of connecting devices to PCBs, is less suited to the application because it would damage the low-temperature substrate. Special conductive pastes are used to overcome this issue; however, the challenge of achieving solder’s low resistivity remains.

SEMI-CONDUCTIVE INKS

The use of conductive inks has allowed development of simple components such as switches, resistors, capacitors, inductors, and antennae. One challenge that still exists is the development of semi-conductive inks for the fabrication of components such as transistors, LEDs, sensors and ICs.

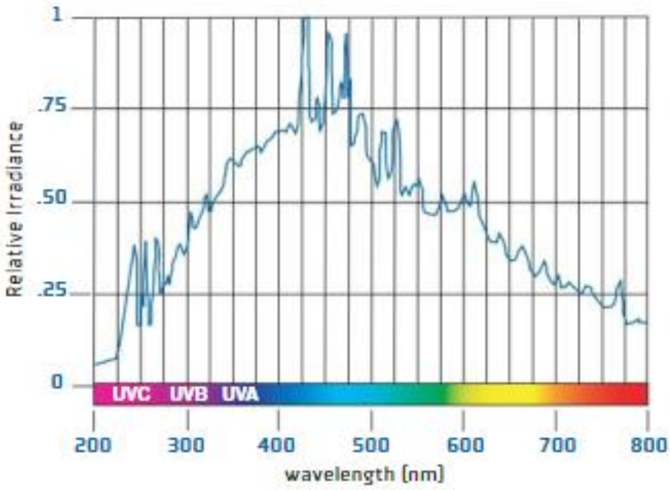

Figure 4 *Spectra of a xenon-arc flash lamp*

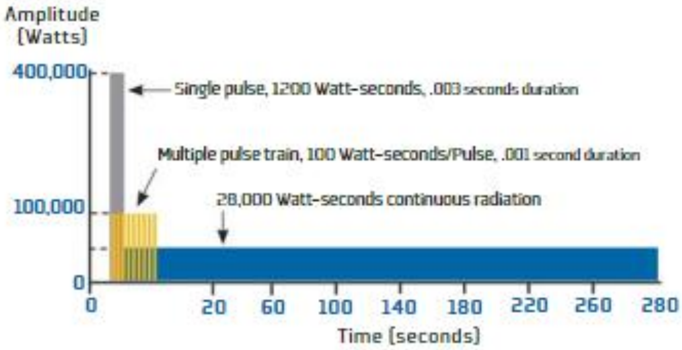

Figure 5 *Pulsed vs. continuous light*

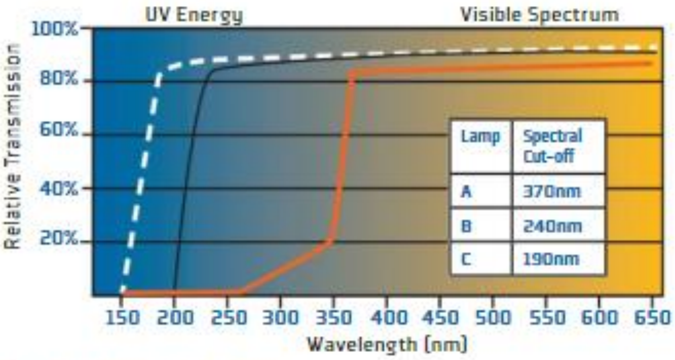

Figure 6 *Envelope cut of spectra*

Bonding conventional, silicon-wafer-based devices to low-temperature substrates is a challenge because these devices typically are rigid. One way to overcome this is to make a silicon wafer sufficiently thin so it too becomes flexible. Wafer thinning can create silicon wafers that are around 50 um thick, allowing them flexibility and enabling direct bonding to the substrate using conductive adhesives.

Organic semi-conductive inks exist, but their use in development of ICS is limited not only by the issues of registration mentioned above, but also by the feature site achievable by the printing process. The simplest functional IC can have hundreds – if not thousands – of transistors, and a silicon wafer can have a footprint a few nanometers. Conventionally printed transistors carry a footprint site in the range of tens of microns at best. Even the simplest IC can take up a few centimeters of real estate in circuits where even a single print defect can produce non-functional results.

Therefore, it does not seem feasible to make fully functional circuits on flexible substrates at this time, but rather more practical to address the issues of bonding silicon wafers and other active components directly onto the substrate that has traces formed by regular printing.

FLASH-LAMP TECHNOLOGY

Flash lamps have the ability to generate light with wide bandwidth spectra, from deep UV to infrared ***(Figure 4)***. High-energy xenon-arc flash lamps can generate high-peak power pulses and are capable of delivering significantly greater peak energies compared to continuous sources like mercury, fluorescent, or halogen lamps by storing energy over time and delivering it as a short-duration, high-intensity pulse. This high-peak pulse energy is sufficient to cause sintering to take place. Xenon-arc lamps generate light by using high voltage to break down the inert gas within the lamp envelope, thereby creating a conductive discharge path where the flash exists.

Very short on times enable flash lamps to deliver high peak photonic power effectively without a dramatic increase in substrate surface temperature ***(Figure 5)***. Typical on times can be in the order of a few microseconds to milliseconds with day cycles ranging from tens of hertz to a few hertz. Peak powers of a few megawatts can be generated in these very short durations. Flash lamps can be tailored for specific applications and deliver repeatable and uniform intensities over a broad spectrum by adjusting voltage and current delivery through the lamp. These are ideal characteristics for sintering applications where adjustment of peak and total energy must be made for different samples. High peak power means greater penetration depth and sufficient energy for useful work-particularly in the case of sintering.

Lamps are manufactured with a low-pressure xenon gas inside a transparent envelope. There are two electrodes, typically made of different materials. The cathode is typically barium doped and designed to have a low work function for the generation of electrons, whereas the anode is usually made of tungsten to sustain the bombardment of electrons during a flash. These lamps do have a polarity, and improper connection of the lamp can cause lamp damage and early lamp failure. Metal particles are deposited on the lamp’s glass as electrodes age or are damaged during normal use. This, as well as other forms of lamp aging, results in a fall-off in intensity.

Lamp life is usually reported in millions of pulses in typical use and is approximately the number of pulses for the lamp to remain within 20% of its initial intensity. This value changes based on the energy of the pulse and cooling. Lamp life can be extended significantly by driving the lamps with lower energy.

The lamp envelope defines the physical lamp profile. The material used for the envelope can define the output spectra from the lamp ***(Figure 6)***. Clear fused quartz (CFQ) is used when deep UV is required, but high-energy flashes from this source can generate significant amounts of possibly undesirable ozone. Alternatives include doped quartz tubes that block UVC and, therefore, do not generate ozone. Envelope thickness, bore diameter, length, and gas pressure are important parameters in defining the optical power that can be generated safely by the lamp. A theoretical limit called the explosion energy for the lamp is a function of some of these parameters and is the energy that can destroy a lamp catastrophically. Typical operation of the lamp is set at 10% of this explosion energy.

Electrons used to drive flash lamps can be quite simple: a high-voltage supply, a storage capacitor, a pulse-forming inductor, and a trigger circuit. However, the system's high power requirements require special designs to account for safety, noise, and power management.

As mentioned earlier, lamp cooling is a very significant component of the optical system and sets the operational limits of the lamp and affects lamp life. Forced air for cooling offers the simplest solution for most applications. Water-cooled flash lamps offer higher power solution, but they tend to be more costly and complex. Maintenance of a water-cooled system is also more complicated and required operators to manage the risks associated with the close proximity of water and high voltage.

PHOTONIC SINTERING IN ROLL-TO-ROLL PRINTING

Simplicity is the key to successful deployment of photonic sintering in roll-to-roll printing. The solution offered by photonic sintering from this perspective looks very attractive. First, we have an ink-deposition phase that lends itself to standard printing processes, followed by a standard ink-drying phase. The only additional step is the photonic-sintering phase, which can be as easy as a retro fit of a flash-lamp system over the printing web. There are no additional process requirements like pressure, special gas, or chemicals.

Dwell time in photonic sintering is not an issue because the reaction is instantaneous as opposed to thermal sintering, which can take minutes. Pulse rate, however, is critical to controlling the overlap of photo-sintered regions and avoiding overexposure or banding when a gap exists between the two adjacent regions. Scalability becomes an important factor from the standpoint of versatility, especially when considering different roll-to-roll speeds and ink formulations. Photonic sintering systems can be scaled easily by increasing the number of lamps required for a given process speed.

A FLEXIBLE SOLUTION FOR NUMEROUS APPLICATIONS

Low-temperature photonic sintering is compatible with a variety of substrates and functional inks, including silver flakes, ITO, and copper, silver, and gold nanoparticle-based inks. The development of new, flexible tools that can help process developers, ink formulators, printing-equipment manufacturers, and end users evaluate the technology rapidly and find solutions for their specific needs is the ultimate key to successful deployment of photonic sintering in the production arena. It is clear that photonic sintering will play a major role in production of flexible electronics and will have far-reaching consequences in the production of electronics and in our everyday lives in the near future.

SAAD AHMED, PH.D.
Xenon Corp.

SaadAhmed is an engineering manager at Wilmington, MA – based Xenon Corp., a developer of pulsed-light solutions for a variety of industries. His expertise incudes R&D, product conceptualization and design, and more. Ahmed earned a Ph.D. in electrical engineering from the University of Liverpool, UK.