https://doi.org/10.2352/ISSN.2169-4451.2017.32.309

Reprinted from
Journal of Imaging Science and Technology® 60(4): 040403-1–040403-5, 2016.

Intense Pulsed Light Sintering of an Inkjet Printed Silver Nanoparticle Ink Depending on the Spectral Absorption and Reflection of the Background

Dana Mitra, Kalyan Yoti Mitra, and Melinda Hartwig
Department for Digital Printing and Imaging Technology, Technische Universität Chemnitz, Germany
E-mail: dana.weise@mb.tu-chemnitz.de

Reinhard R. Baumann▲
Department for Digital Printing and Imaging Technology, Technische Universität Chemnitz, Germany
Printed Functionalities, Fraunhofer Institute for Electronic Nano Systems ENAS, Chemnitz, Germany

Abstract. *The development of novel manufacturing methods for flexible, light weight and cost-efficient electronics has attracted great interest in recent years. The inkjet printing technology is an attractive fabrication process due to its additive, high precision and up-scalable deposition process. One of the key components of printed electronic devices is the conductive track. A major requirement is a desired and device dependent electrical performance induced by an appropriate post treatment process. Here, the novel method of using intense pulsed light (IPL) to convert printed liquid films into solid and functionalized metallic layers has great potential when it comes to fabrication of electronics on thin, flexible and even stretchable polymeric foils. Within this research, the IPL sintering and its dependence on the spectral absorption and reflection of various materials is investigated. A nanoparticle silver ink is inkjet printed on a transparent PET foil. Afterwards, the printed samples are placed at a defined distance from the background inside the photonic sintering equipment and flashed on one hand with various flashing parameters and on the other with changing background materials and colors. Changing the background color influences the reflection and absorption properties of the flashlight; the electrical performance of the IPL processed conductive layers can be drastically changed when such a phenomenon occurs. Highly conductive silver tracks or electrodes can be manufactured on thin and flexible polymeric substrates without damage.*

INTRODUCTION

To convert printed liquid patterns/films into solid functional films with the desired microstructure as well as electrical performance, a thermal post treatment is required. Within this, solvents are evaporated, stabilizing additives and all the organics are cast out and the metallic nanoparticles (NPs) merge together.[1] In most cases, high temperatures are required, which makes this process unsuitable for the thermally instable polymeric foils.[1–4] In order to achieve the desired electrical performance even on ultrathin, flexible and stretchable substrates, which cannot withstand high temperature treatments, novel sintering methods need to be introduced. These technologies constitute the usage of, e.g., lasers,[5–7] infrared (IR) radiation[5,6,8] or microwaves,[5,6,9] and the method of intense pulsed light (IPL) sintering has also been introduced as an alternative.[5,6,10–13]

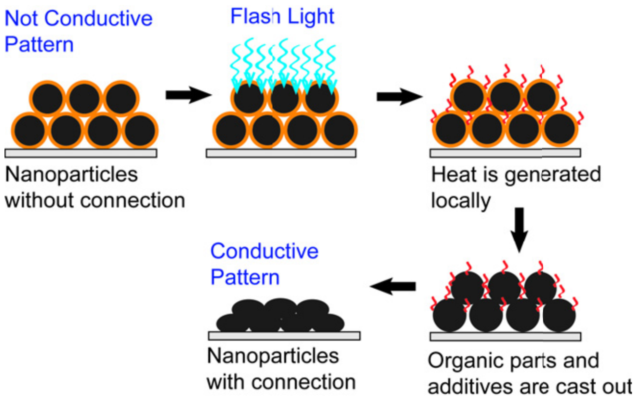


Figure 1. The basic process of IPL sintering of an NP metal layer.

The basic process is demonstrated in Figure 1. By selectively irradiating the samples with high intensity light flashes only over the dark NP metal ink films, the energy (light) in the form of heat is absorbed by this ink film. Polymer foils are, due to their transparency, not affected by the light and hence are not directly heated. The process of photonic sintering is in the range of microseconds (μs) to milliseconds (ms). Even a drastic increase in temperature inside the printed metal layer only lasts for a few ms, which is theoretically too fast to affect the subjacent substrate. Nevertheless, this heat impact has to be taken into account at the border of the heated metal layer and the polymer substrate.[14]

The major factors influencing the IPL sintering are the intensity of the light and the optical properties of the materials (substrate and ink) themselves. On one hand, the absorption rate of the printed films and, on the other hand,

▲ IS&T Member.

Received Mar. 2, 2016; accepted for publication May 25, 2016; published online July 1, 2016. Associate Editor: Branka Lozo.

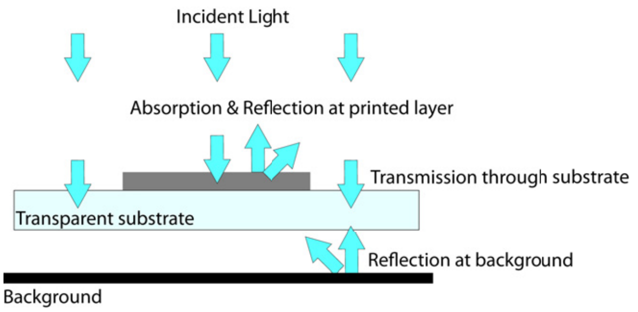


Figure 2. Graphical description of possible absorption and reflection schemes of a printed metal layer on a transparent substrate with 3 mm distance to a colored background.

the absorption and reflection rates of the substrate and surroundings have to be considered (Figure 2).

A metal film is directly heated by the absorbed light, but could be also indirectly influenced by reflected light from the surroundings.[15] From Fig. 2 it is seen that the light is transmitted through a transparent substrate, but the material underneath is not transparent. The sintering system used in this work (see Materials and Methods) has a closed setup (housing), where light flashes are irradiated from the top via xenon flash lamps and possibly get reflected by the walls and especially by the background of the machine.

MATERIALS AND METHODS

The silver nanoparticle ink used in this work was UTDAgIJ1 (UT Dots, Inc.). The basic substrate was a transparent poly(ethylene terephthalate) (PET) foil (Melinex® 401 from DuPont Teijin Films) with a thickness of 100 μm. The substrate was cleaned with ethanol and compressed air before printing. Printing was carried out with a Dimatix Materials Printer (DMP 2831 from Fujifilm Dimatix) with 10 pL printheads. The print pattern consisted of squares of 5 mm × 5 mm dimensions as well as narrow lines of 5 mm length and 3 pixel width (3 pixel means three single dot lines at a distance of 40 μm and therefore merging to one narrow line) for the investigation of the electrical characteristics by means of sheet resistance measurements, visual characterization by a light microscope and a surface profile analysis with a Dektak. The printed samples were dried in an oven at 80°C for 10 min. Flashing was carried out with a PulseForge 3200 from Novacentrix. This flash lamp was integrated in a hybrid R2R modular printing machine from 3D-Micromac AG, which enables inline printing and sintering on an industrial scale. The dependence on the light absorption and reflection during the IPL processing was analyzed by varying the background base beneath the transparent PET foil (Figure 3).

Three types of paper with varying spectral absorptions and coatings were used to investigate whether the sintering effect of NP silver ink films can be enhanced by varying the light reflection. One was an uncoated paper with either black or red color and the other one was a coated glossy white paper. The distance between the sample and the

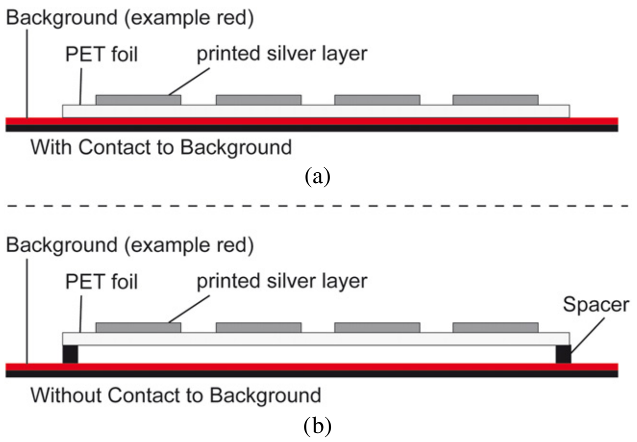


Figure 3. Graphical description of the experimental setup: (a) with direct contact with the colored background; (b) without direct contact with the colored background.

underground was set to 3 mm for the setup without contact with the background.

The flashing energy was varied and the impact on the electrical and optical characteristics was systematically analyzed. The research included microscopic images (light microscope DM4000, from Leica), surface profiles by surface topographic scan with mechanical contact (profilometer Dektak 150 by Veeco) and electrical measurements (sheet resistance by a four-point method with a manual probe system PM5, Süss Microtec) to prove whether changing the background materials showed an impact on the electrical and optical performance. Spectral analysis (TIDAS MSP 800, J&M Analytik AG) was carried out for the light absorption and reflection of the background base materials and then compared with relation to the results of the characterized silver films.

RESULTS AND DISCUSSION

Spectral Reflection and Absorption

The first investigation was on the absorption and reflection of the varied background materials as a basis for the experiments and results interpretation. It was found that on a coated white paper the highest reflection and the lowest absorption rate can be measured, whereas an uncoated black paper has the lowest reflection and highest absorption rate among the background materials used.

Optical Analysis

In Figure 4, microscopic images of UT Dots silver lines printed on PET and flashed with a lower energy density of 0.96 J/cm^2 are presented. It can be seen that the silver lines flashed with the red as well as the white background show a slight dark border (Fig. 4(b) and Fig. 4(c)). In the magnification of the line border for the white background a small crack along the line is visible.

In the surface profiles (Figure 5), this darker border turns out to be a formation of a hill and a valley at both edges of the silver line flashed with the red and white backgrounds

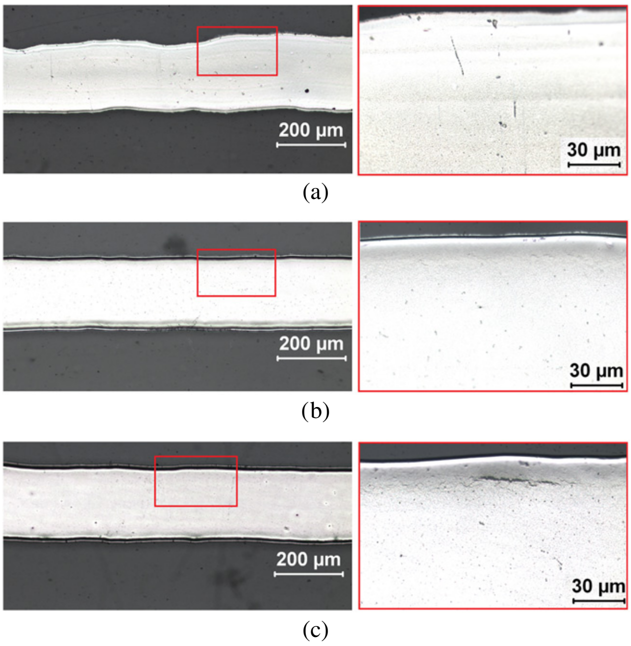


Figure 4. Microscopic images of printed and flashed (0.96 J/cm^2) silver lines without contact with the background: (a) black background; (b) red background; (c) white background.

(Fig. 5(b) and Fig. 5(c)). The hills have a height of around 1.5 µm and the valleys a depth of around 0.3–0.8 µm for the background colors red and white. The silver line with the black background has an average height of ~0.3 µm, whereas the average heights for the red and white backgrounds are increased to 0.4 µm and 0.5 µm, respectively. The silver line flashed with the black background does not have this characteristic. It is therefore concluded that the black background seems to absorb a greater amount of light energy and therefore results in a lower energy density within the photonic sintering process, which causes reduced damage of the silver patterns (lines as well as squares), whereas the red and white paper, but especially the white paper, reflect a greater amount of light energy and therefore enhance the energy density inside the photonic sintering process, and therefore also enhance the sintering temperature and cause the characteristic defects. These cracks occur especially at the boundary between the silver and the PET foil. The reason could be the thermal impact on the temperature instable PET foil at this boundary.

On analyzing the images that refer to the printed layers flashed with a higher energy density (1.25 J/cm^2), the cracks at the borders of the silver lines are clearly increased and are visible for the red and white backgrounds (Figure 6(b) and Fig. 6(c)). Optically, the samples with the black background also present a slight black border around the silver line (Fig. 6(a)), but the magnification still shows no crack formation here.

In the surface profiles, a hill formation for the samples with the black background with up to around 1.3 µm was observed (Figure 7(a)). However, no valley and therefore no crack inside the PET foil could be noted from the profiles.

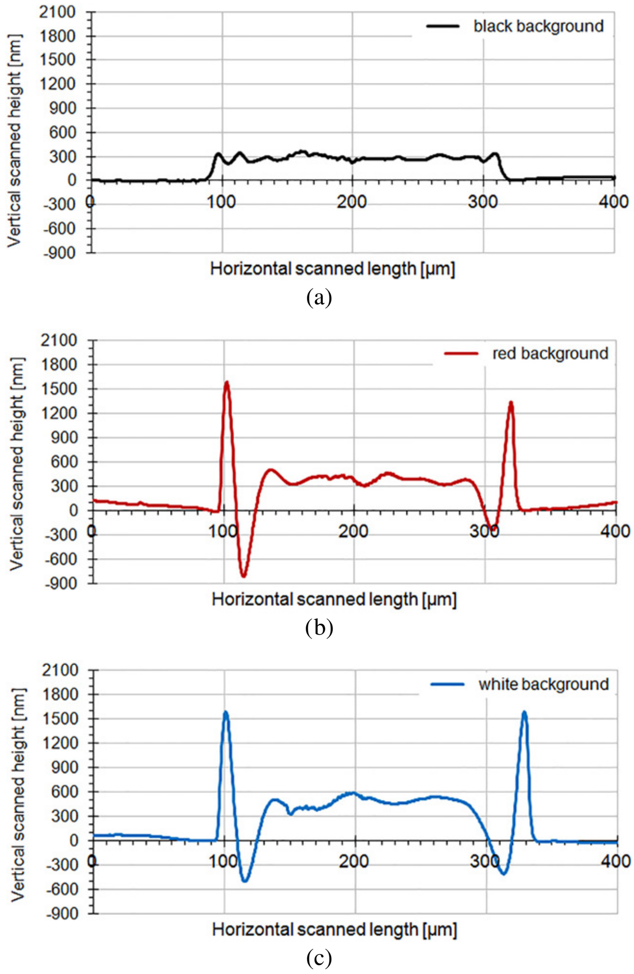


Figure 5. Surface profiles scanned over a single silver line after flashing with 0.96 J/cm^2 without direct contact with the background: (a) black background; (b) red background; (c) white background.

The profiles over the lines for the red and white backgrounds (Fig. 7(b) and Fig. 7(c)) were comparable to the ones with the lower energy density of 0.96 J/cm^2 (Fig. 5(b) and Fig. 5(c)). In conclusion, for the black background, an impact on the silver lines could be observed, resulting in a hill formation at the edges, but still no crack formation.

Electrical Analysis

Apart from the optical investigation, the main focus is laid on the electrical characteristics of the flashed samples and whether an effect on the sintering effect can be achieved by varying the spectral absorption and reflection of the background (Figure 8).

It was found that the white background resulted in the least sheet resistance for both setups, which were with and without contact with the background (Fig. 3). This can be explained by two reasons. One is the high reflection of the white color in general, but also the white paper had a glossy coating, which additionally enhanced the light reflection. As expected from the black colored background paper, the sheet resistance was drastically increased or the sintering was not

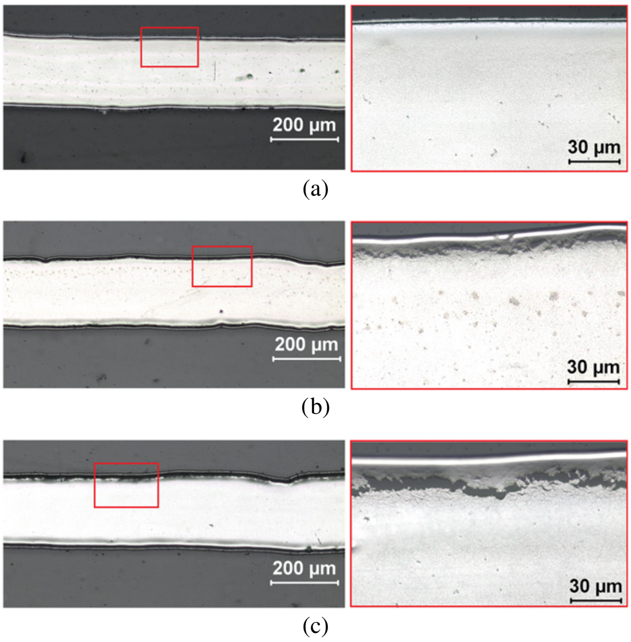


Figure 6. Microscopic images of printed and flashed (1.25 J/cm^2) silver lines without contact with the background: (a) black background; (b) red background; (c) white background.

sufficient at all to form conductive structures. Interpretations could be made that the darker material absorbs more and reflects less light, and therefore leads to a minor sintering effect.

For both setups (with and without contact), the sheet resistance decreases with increasing energy density of the flash lamp. At the highest energy density used of 1.25 J/cm^2, the background color shows minor impact on the sheet resistance. For example, in the setup without contact with the background (Fig. 8(b)), the sheet resistances for the white, red and black backgrounds are $0.28 \pm 0.02\ \Omega/\square$, $0.3 \pm 0.17\ \Omega/\square$ and $0.55 \pm 0.03\ \Omega/\square$, respectively. Taking into account the crack formation for the white and red background colors, the black background resulted in comparable low sheet resistance without any crack formation at the same energy density.

CONCLUSIONS

A nanoparticle silver ink was inkjet printed on a 100 µm thin PET foil and IPL sintered with various energy densities. The background color of the flashing system was varied from highly reflective glossy white paper to uncoated (not glossy) red and black paper. The samples were flashed with direct contact or a gap of 3 mm to the background.

It was found that the highly reflective white background resulted in low sheet resistance at comparable lower energy densities of 0.96 J/cm^2, whereas the samples on the black background did not present conductivity at all at this energy density. Increasing the energy density to 1.25 J/cm^2 results for all of the background colors in sheet resistances below $1.5\ \Omega/\square$ for the with contact setup and below $0.6\ \Omega/\square$ for

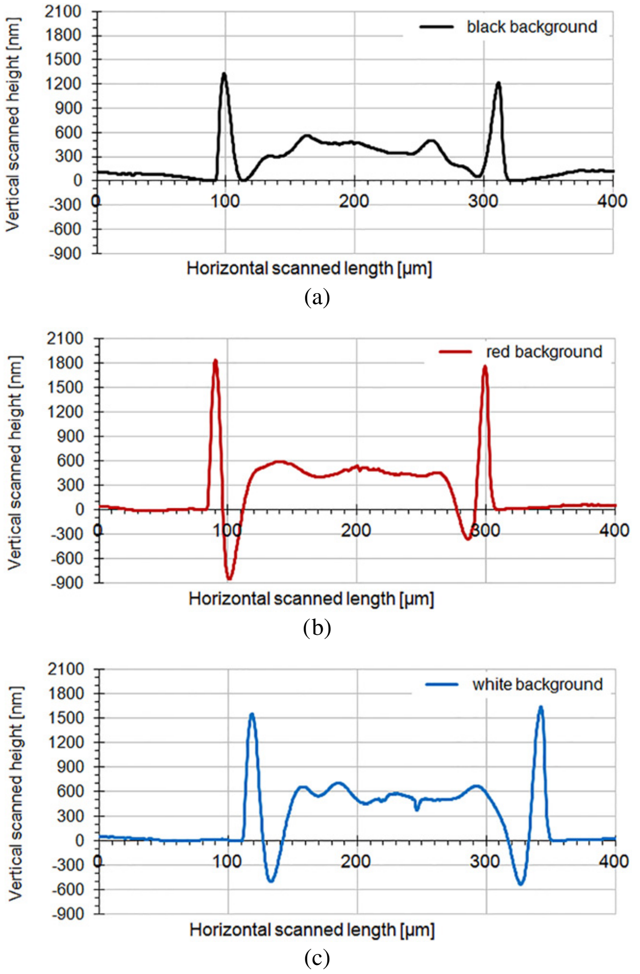
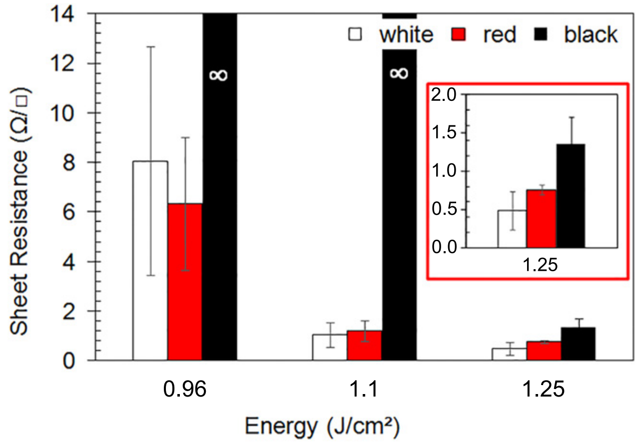


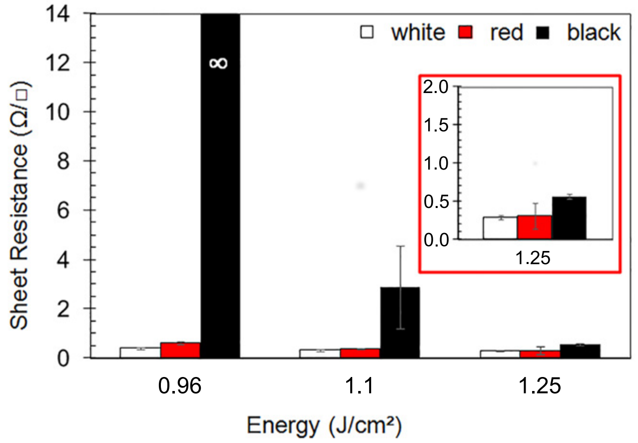
Figure 7. Surface profiles scanned over a single silver line after flashing with 1.25 J/cm^2 without direct contact with the background: (a) black background; (b) red background; (c) white background.

the without contact setup. It was demonstrated that a highly reflective background increases the sintering and therefore increases the conductivity of the samples compared with a highly absorbing black background. However, the use of higher light energy densities results in minor differences in the sheet resistance between the background colors. Although with the highly reflective white background, on the one hand, the lowest sheet resistance at lower energy density could be achieved, defects like cracks inside and delamination of the silver layer were observed, which are not feasible for printed electronic applications. No defects in the silver layers were obtained for the black background even with higher energy densities, but it resulted in a similar low sheet resistance and therefore was more suitable for printed electronic applications. It is of major importance to find the right balance between absorption and reflection in relation with the flashing energy to achieve optimal results.

In conclusion, the background color of the substrate holder has a major influence on the electrical performance and the defect formation for the intense pulsed light sintering process.



(a)



(b)

Figure 8. Measured sheet resistance of silver films in dependence on flashing energy and background: (a) with contact; (b) without contact.

ACKNOWLEDGMENT

This research work was financially supported by the BMBF funded project "EPOS" (FKZ: 03EK3529K) and the DFG funded project "Stabilization of microsieves" (FKZ: BA 1169/7-1).

The authors thank Svetlana Perepadan Jose (TU Chemnitz, Digital Printing and Imaging Technology) for her experimental support in printing and characterization.

REFERENCES

1. J. R. Greer and R. A. Street, "Thermal cure effects on electrical performance of nanoparticle silver inks," Acta Mater. **55**, 6345–6349 (2007).
2. H. Klauk, "Organic electronics, materials," *Manufacturing and Applications* (Wiley-VCH, 2006).
3. D. J. Lee, J. H. Oh, and H. S. Bae, "Crack formation and substrate effects on electrical resistivity of inkjet-printed Ag lines," Mater. Lett. **64**, 1069–1072 (2010).
4. K. Ryu, Y.-J. Moon, K. Park, J.-Y. Hwang, and S.-J. Moon, "Electrical property and surface morphology of silver nanoparticles after thermal sintering," J. Electron. Mater. **45**, 312–321 (2016).
5. J. Perelaer and U. S. Schubert, "Novel approaches for low temperature sintering of inkjet-printed inorganic nanoparticles for roll-to-roll (R2R) applications," J. Mater. Res. **28**, 564–573 (2013).
6. S. Wünscher, R. Abbel, J. Perelaer, and U. S. Schubert, "Progress of alternative sintering approaches of inkjet-printed metal inks and their application for manufacturing of flexible electronic devices," J. Mater. Chem. C **2**, 10232–10261 (2014).
7. J. Niittynen, R. Abbel, M. Mantysalo, J. Perelaer, U. S. Schubert, and D. Lupo, "Alternative sintering methods compared to conventional thermal sintering for inkjet printed silver nanoparticle ink," Thin Solid Films **556**, 452–459 (2014).
8. E. Sowade, H. Kang, K. Y. Mitra, O. J. Weiss, J. Weber, and R. R. Baumann, "Roll-to-roll infrared (IR) drying and sintering of an inkjet-printed silver nanoparticle ink within 1 second," J. Mater. Chem. C **3**, 11815–11826 (2015).
9. J. Perelaer, B. J. de Gans, and U. S. Schubert, "Ink-jet printing and microwave sintering of conductive silver tracks," Adv. Mater. **18**, 2101–2104 (2006).
10. H. Kang, E. Sowade, and R. R. Baumann, "Direct intense pulsed light sintering of inkjet-printed copper oxide layers within six milliseconds," Appl. Mater. Interface **6**, 1682–1687 (2014).
11. J. Niittynen, R. Abbel, M. Mantysalo, J. Perelaer, U. S. Schubert, and D. Lupo, "Alternative sintering methods compared to conventional thermal sintering for inkjet printed silver nanoparticle ink," Thin Solid Films **556**, 452–459 (2014).
12. D. Weise, C. Sternkiker, and R. R. Baumann, "Intense pulsed light sintering and parameter optimization of various inkjet printed silver electrodes," *Proc. IS&T NIP31: 31st Int'l. Conf. on Digital Printing Technologies and Digital Fabrication 2015* (IS&T, Springfield, VA, 2015), 2015, pp. 62–65.
13. N. Marjanovic, J. Hammerschmidt, J. Perelaer, S. Farnsworth, I. Rawson, M. Kus, E. Yenel, S. Tilki, U. S. Schubert, and R. R. Baumann, "Inkjet printing and low temperature sintering of CuO and CdS as functional electronic layers and Schottky diodes," J. Mater. Chem. **21**, 13634–13639 (2011).
14. D. Weise, K. Y. Mitra, E. Sowade, and R. R. Baumann, "Intense pulsed light sintering of inkjet printed silver nanoparticle ink: influence of flashing parameters and substrate," *MRS Proc.* (Boston, 2015), Vol. 1761, doi:http://dx.doi.org/10.1557/opl.2015.680.
15. I. Reinhold, M. Müller, M. Müller, W. Voit, and W. Zapka, "Spectrally enhanced photonic sintering," *Proc. IS&T NIP28: 28th Int'l. Conf. on Digital Printing Technologies and Digital Fabrication 2012* (IS&T, Springfield, VA, 2012), vol. 2012, pp. 424–430.