Spectrally Enhanced Photonic Sintering

Ingo Reinhold, Matthias Müller, Maik Müller, Wolfgang Voit, Werner Zapka; XaarJet AB, Järfälla, Sweden

Abstract

Inkjet printing with silver nanoparticle inks is frequently being used to print electrically conductive structures. However, typically slow thermal post-processes are applied to produce metallic contact between the nanoparticles resulting in the high electrical conductivity. In an earlier evaluation a number of different post-process were investigated for their capability to sinter the inkjet printed structures within such short time frame to allow for integration into roll-to-roll or roll-to-sheet machines. Among the different techniques like IR-irradiation, and Rapid Electrical Sintering, Photonic Sintering appeared as the most prominent candidate, and was shown to enable electrical conductivities equal to oven sintering. In that previous investigation the inkjet printed structures were dried and subsequently shipped for off-line post treatment.

The hybrid process of inkjet printing of silver nanoparticle inks and photonic sintering was further investigated with the goal to implement both processes on a roll-to-roll machine. Specifically it was attempted to perform the photonic sintering process with a single lamp and without an intermediate drying process.

In this paper we investigate the sintering characteristics of an inkjet printed, wet deposit having liquid volumes of 510 pL per 100 μm^2 on non-absorbing substrates using a single Xenon Sintering 2000 system. The paper specifically highlights the importance of radiation homogeneity, threshold energy, substrate and track morphology onto the sintering process. The influence of the spectral composition of the light is analyzed. The findings allow for spectral tailoring of the process to successfully work on PI and PET irrespective of the illumination source.

Introduction

Producing conductive features using printing technologies has attracted great interest within the electronics community, as these highly productive processes are applicable to generate functional structures using reasonable, but sufficient resolution. Providing pattering in a purely additive fashion, which reduces the necessity for multi-step photolithographic processes, is thereby of high importance. While the highest productivity can be obtained using conventional rotary techniques, such as offset, gravure, screen and flexo-printing, some applications show particular interest in fully digital patterns, which enable a quick re-definition of the product on the machine without the need for changing the permanent print master.

With the advance of the production of metal nanoparticles and their capping to form stable dispersions, inkjet printing was shown to be a viable application technique, though being limited in the applicable viscosities to the range of 1-20 mPas, limiting the solid loading of solute and therefore the final thickness of the feature when applied to the substrate. The materials deposited with inkjet include among others silver nanoparticles, coated copper nanoparticles, copper oxide nanoparticles as well as indium tin oxide nanoparticles.

While deposition was shown for many different specimen of the inks mentioned, the major challenge for a commercial application of these kinds of processes are the annealing or sintering processes, which render the deposited non-conductive, wet feature back into a metallic element with electrical characteristics reasonably close to that of the bulk material. Several processes were proposed to achieve this in a low-temperature regime motivated by the application of the low cost substrates. Suitable processes presented in the literature include convective oven sintering, microwave sintering, plasma sintering, laser and IR radiation [1], chemical sintering [2,3] as well as broadband photonic sintering. Many of the results presented were achieved utilizing some means of drying in-between the printing and sintering step, which was implemented by either applying a type of thermal energy (i.e. IR drying, oven drying) or the application of special porous substrates, which act as a dryer by depleting the solvent from the wet deposit and introduce partial degradation of the nanoparticles' polymeric shells by acidic components [4].

While most techniques exemplify their potential for the fast generation of conductive features from inkjet-printed deposits, they typically lack the potential for roll-to-roll manufacturing, which is highly anticipated in the community. So far, photonic sintering and derived hybrid processes show the sintering speed needed but rely on the presence of a dried deposit. Only recently approaches were presented that employ the energy from a photonic sintering system for the inline drying and sintering of flexo- and inkjet printed structures [5] using a multi-lamp arrangement at substrate velocities of 5 – 15 m/min.

Experimental

The experiments presented were performed using a Xaar126-50 pL printhead in conjunction with an optimized waveform for the silver ink EMD 5603 (SunTronic, SunJet, UK). Printing was carried out on a heatable X-Y-stage performing at an accuracy of 1 µm in positioning in order to give highly repeatable results. The printhead was operated at an equidistant resolution of 70.55 µm in X and Y direction by tilting the printhead by 59.04° [6]. The substrate temperature was chosen to be 70 °C for all substrates in order to give acceptable line formation on all different substrates and keep the evaporative loss of solvent constant throughout all experiments.

Sintering was performed using a Sinteron 2000 unit (Xenon Corp, US) in combination with linear emitters mounted in circular and oval reflector housings in order to provide homogeneous or focused irradiation of the samples. The flashing frequency of the unit was set using a Krohn-Hite 5400 signal generator. The intensity characteristics were studied using general-purpose thermal fax paper, which was digitalized using an Epson Perfection 1640 scanner and analyzed using ImageJ [7]. In order to allow for consistency, all experiments presented below were conducted at the maximum of the intensity characteristics of the respective reflector.

Online monitoring of sintering was performed using a two-point measurement of the resistance of the deposit between sputtered gold electrodes with a fixed distance of 20 mm, using an HP 34970A data acquisition unit (Hewlett Packard, US) connected to two tungsten tips (Karl Süss, US). Synchronization of experimental data was achieved by monitoring the current of the sintering unit using 2 extra channels of the acquisition unit.
Sintering experiments were carried out on polyimide (PI), poly(ethylene terephthalate) (PET), polycarbonate (PC), poly(ethylene-2,6-naphthalate) (PEN), polypropylen (PP). LED connections were performed on RMPD® substrates consisting of two layers, a basic one accommodating the LED chips and a fitted one to accommodate the via connections with a depth of 25-45 µm.

Lamp Intensity Profiles

The intensity profiles depicted in Figure 1 were recorded by exposing the underlying fax paper to two flashes of 510 J and were normalized to the maximum gray level found in the specimen after digitalization. The plot clearly shows the difference of the reflectors with respect to the energy distribution alongside with the clearly visible minima and maxima. For the circular reflector the maxima are located roughly 1 – 1.5 cm from the centerline of the lamp, while in the case of the oval reflector the expected focus is visible, which narrows the working range to a maximum of 1 cm. An interesting phenomenon is the flattening of the 5 mm line for the circular and the 25 mm distance of the oval reflector, which indicates the saturation of the paper and therefore does not represent the real intensity distribution.
This inhomogeneity in the intensity profile is expected to be crucial for the process, as it defines the maximum energy forwarded to the substrate and may result in overheating, strong temperature gradients between the deposit and the surrounding, explosive evaporation and, therefore, disadvantageous electrical characteristics of the resulting structures.
In order to estimate the performance of such a sintering system, experiments were repeated with lower energy to facilitate the reduction of the saturation of the paper and provide a more quantitative image of the distribution. These acquired intensity distributions *D(x)* were used to predict the performance of the lamp by estimating the lateral exposure level across the sample (*EXP*) as a multiple of the maximum intensity of a single shot with taking the substrate velocity v_s and the flashing frequency of the lamp f into consideration. Assuming linear superposition and negligible movement during exposure we find the level for the finite amount of flashes n_f by

$$EXP(x) = \sum_{n=1}^{n_f} D\left(x - \frac{v_s}{f} \right)$$

Figure 2 shows a calculation using different frequencies and substrate velocities in order illustrate the potential application. The solid horizontal lines in the graphs represent the optimum setting,

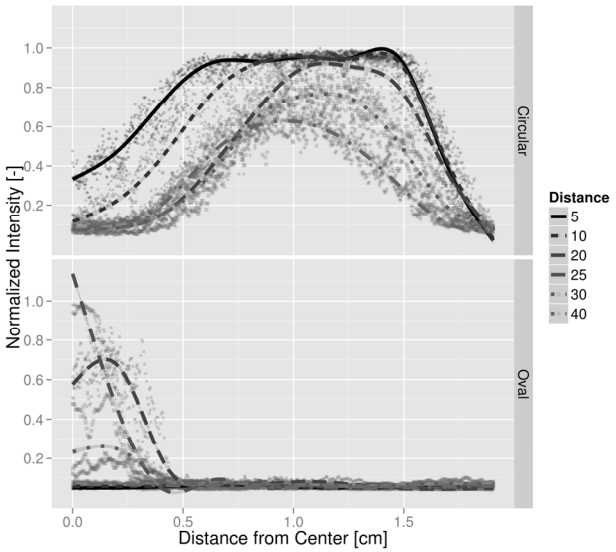


Figure 1: Intensity profiles from a circular (top) and an oval (bottom) reflector assessed from the reflector center at various distances from the lamp housing [two flashes with 510 J, pulse width 0.58 ms, lines represent predictions of a moving average model]

which was found during the experiments and will be elucidated later. It is evident from the image, that none of the combinations of the settings is capable of reaching the desired performance. Furthermore, the fluctuations visible for substrate velocities higher than 0.01 m/s suggest that the applied energy will vary over the substrate and, hence, inconsistent electrical characteristics are to be expected along the sample. This is more pronounced for the oval reflector but simply originates from the double peak spectrum of the circular arrangement. This prediction had to be treated with care, as the non-zero center intensity of the circular reflector may mathematically generate high intensities, while the actual heating effect will strongly differ from a single flash with an equivalent intensity.
A solution to this is to increase the repetition frequency of the illumination source in order to illuminate more often at lower power, as it was discussed and implemented by Teunissen *et al.* [5]. Homogenizing the circular reflector characteristics may be an alternative approach to gain homogeneous characteristics with lower repetition frequencies. Simple stacking of illumination sources appears rather critical, as the intermediate cooling of the substrate/deposit will have a strong effect on the efficiency of wet sintering. If appropriate conditions are found to conduct complete drying with the first lamp, higher intensity illumination in the second lamp will generate optimal results.

Wet Sintering

Wet silver ink deposits were manufactured by printing 4 pixel wide lines on PI substrates using 3 passes. The samples were thereafter instantly transferred to the sintering equipment, leaving no time for extensive evaporation. The chosen ink did not allow for drying of printed specimen under ambient conditions.

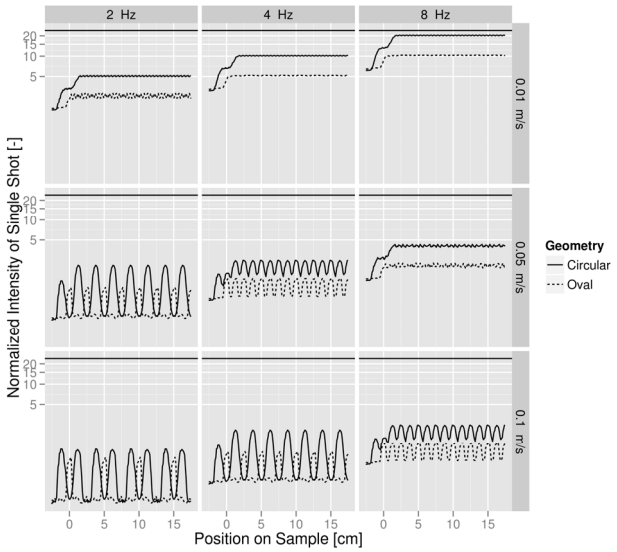


Figure 2: Emulation of the exposure level along a substrate by a single Xenon flash lamp using circular and oval reflectors at different lamp frequencies and different substrate velocities [350 J pulse energy, pulse width 0.58 ms, horizontal line at 24 represents the optimum intensity found in this investigation]

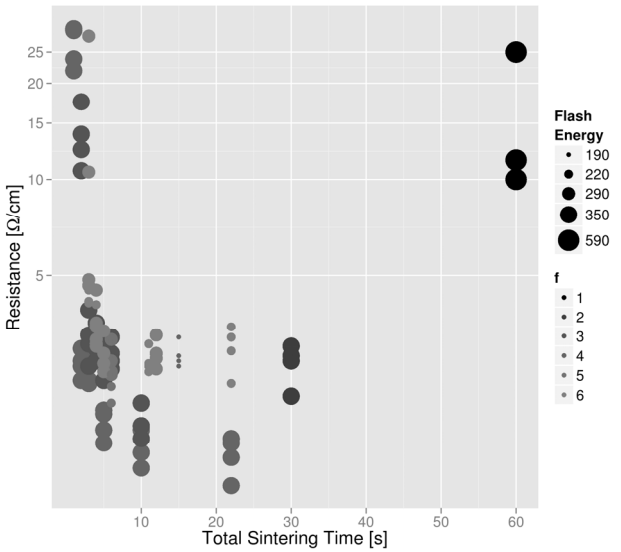


Figure 3: Influence of the energy per flash, the lamp repetition rate and the time used for wet sintering on the final resistance of a 4 px wide silver line on PI [circular reflector (sample placed in maximum, cf. Figure 1), distance to housing 20 mm, pulse width 0.58 ms]

Figure 3 summarizes the influence of the energy per flash, the repetition frequency and time used for sintering in combination with a circular reflector. Combinations yielding non-conductive structures were omitted from the graph.

As can be seen from the graph, resistance values below 30 Ω/cm were achieved, while many combinations yielded resistances even below 5 Ω/cm. The variations within different settings originated from the inhomogeneous intensity distribution in the illumination. For high flash energies of 590 J, only very low frequencies and rather long sintering times of 60 seconds were viable, as otherwise extensive heating rates tended to superheat the solvent and result in ragged tracks with only a few percolation paths available for charge conduction. Very low initial energies of 190 J required higher frequencies and higher numbers of flashes, as energy had to be accumulated in the deposit in order to drive off the solvent and heat the structure sufficiently without too much intermediate convective cooling. In addition there also appeared a dead time < 2 s, where none of the investigated settings yielded sufficient conductivity.

Based on these observations it is postulated that a minimum energy flux into the sample is required in order to render the wet deposit conductive. It was seen that by trading off frequency for energy and vise versa, structures of high conductivity could be generated within less than 10 seconds. An optimum setting was found using a flash energy of 350 J at a repetition frequency of 3 – 4 Hz. With this setting short sintering times of as low as 2 seconds yielded resistance values of 4 Ω/cm. Increased sintering time did not result in degradation of the conductive tracks and improved conductivity towards a very narrow distribution around 2 Ω/cm, as depicted in Figure 4.

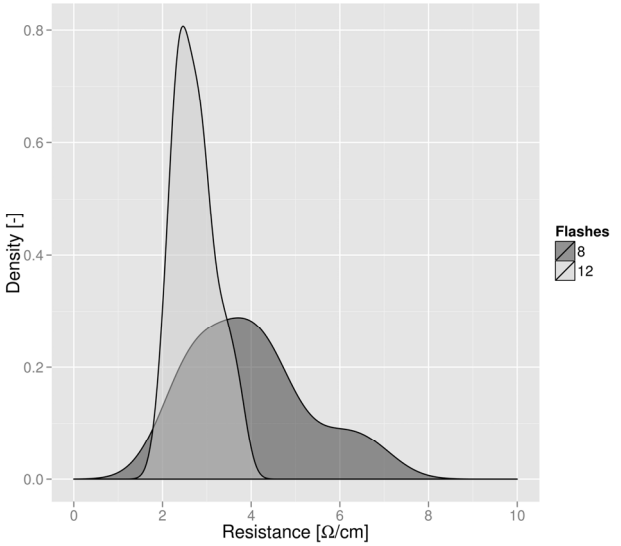


Figure 4: Comparison of repeatability of wet photonic sintering using 4 px silver lines on PI compared between 2 and 3 seconds of exposure [circular reflector, distance to housing 20 mm, flash energy 350 J, pulse width 0.58 ms, repetition rate 4 Hz]

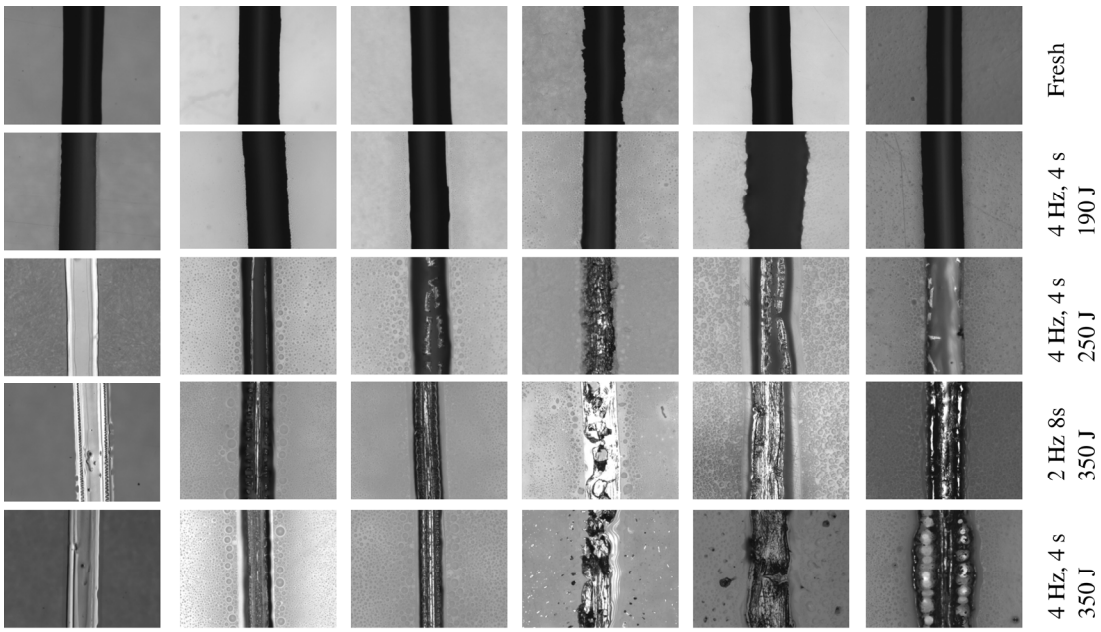


Figure 5: Comparison of the response of a wet 4 px silver line deposited on different materials to different heating rates during wet sintering

Influence of the Substrate

Figure 5 depicts the influence of the substrate used and the heating rates applied. The line conformation on the different substrates was held constant owing to the chosen substrate temperature of 70 ºC except for the samples of PEN, which deviated from the other results due to high surface roughness of the material.

When heating the samples slightly with 190 J at a repetition rate of 4 Hz for 4 seconds no sintering effect was observed and a flow of the fluid on the surface was introduced yielding a contraction in the case of PEN and a spreading of the deposit on PET. When increasing the energy flux into the sample by increasing the energy to 250 J per flash, all substrates exhibited a change in the track conformation alongside with, except for the PI sample, a beginning deposition of fluid in the vicinity of the track. Furthermore, the track outlines became more ragged for most substrates as the tracks started to contract and evaporate their solvents. Upon a further increase in the heating rate through application 350 J per flash, the contraction and partial necking of the tracks became more pronounced. This indicated that the wetting characteristics upon heating had a very strong effect in the wet sintering of the structures as rapid heating generated strong driving forces due to strong local gradients between the temperature of the deposit, the surrounding air and the temperature of the underlying substrate. This behavior peaked in the last setting depicted, where 350 J were applied at a repetition rate of 4 Hz for 4 seconds, leading to full disintegration of tracks on PEN, PET and PP.

An interesting observation was that PI appeared to be the only substrate not showing the *sweating* effect. As PI is the only non-transparent substrate, partial absorption of the incident radiation was to be expected, which in turn resulted in slight heating of the material. It would thereby relief the temperature gradient between the deposit and the substrate and would not allow for condensation of the evaporated solvent from the ink or the outgassed remnants of fluids trapped in the polymer matrix.

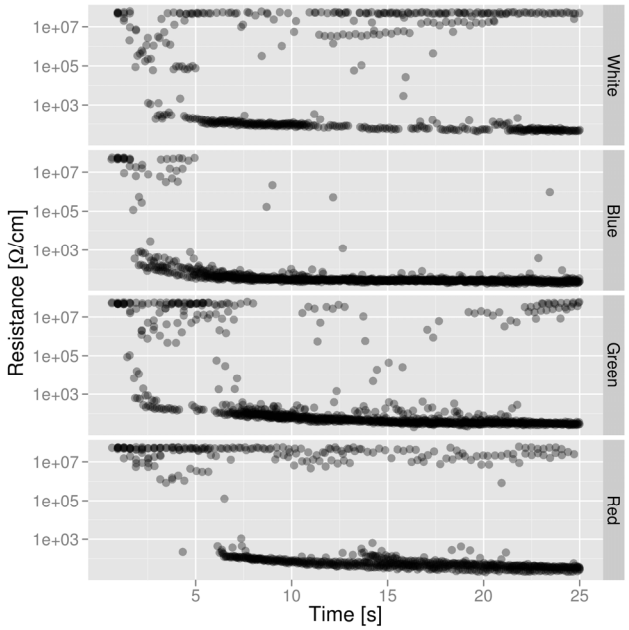


Figure 6: Influence of spectral characteristics of the substrate holder on the evaluation of resistance evolution during wet [circular reflector, distance to housing 20 mm, flash energy 350 J, pulse width 0.58 ms, repetition rate 2 Hz, acquisition frequency 3.2 Hz, 5 samples per spectrum]

Sintering Dynamics

Sintering dynamics were studied by sputtering gold electrodes onto PI substrates with a defined gap of 20 mm. Silver lines were printed in triple pass with a width of 4 pixels.

Figure 6 depicts the results of an experiment employing differently layered substrate holders in order to investigate the influence of

the spectral characteristics of the background. The authors considered this as important as the reflection from the background would resonate as diffuse light in the processing chamber and contribute to the overall process, increasing the process efficiency but potentially also have negative implications. The experiments were conducted at low repetition rates of 1.9 Hz and, therefore, reduced the cumulative heating effect and showed the influence of the spectral compositions of the incident light.

As can be seen, all different colors showed more or less consistent sintering over the monitored period. An interesting point was the performance of the samples with a blue background, implying that only the blue part of the spectrum is repeatedly reflected, showed a higher degree of conformity of the resistance value after the initial drop compared to all other spectral compositions. Nanoparticles having sizes below 50 nm typically have a very strong absorption in the wavelengths shorter than 450 nm. As the ink absorbs energy, drives off solvent and starts the process of Ostwald ripening of the silver particles into larger agglomerates, their absorption characteristics increase dramatically in the blue part of the spectrum and additionally shifts towards the red part of the spectrum [8]. As mainly the blue part remained as resonating radiation, this resembled an optimal process as more power was absorbed and converted into thermal energy due to the larger particle radii, while the low flashing frequency enabled sufficient cooling to inhibit overheating.

A further indication for this theory was visible when a red reflector was used in the system, where the initial drop-off was delayed by 5 seconds due to the low intensity of the blue spectrum. It was assumed that the single transmission of the full spectrum in conjunction with the resonating red portion of the spectrum triggered a slow growth of particles as well as a slight heating of the substrate and the deposit until some initial particle clusters became large enough to absorb the red part of the spectrum. This instantly sintered the track but also overheated due to the stronger absorption. It is well known that the spongy network formed during sintering often exhibits pores and particles in the range of 100 – 200 nm.

The white reflector combined the characteristics of the blue and the red reflector making it most efficient, but also very critical when it came to excessive energy flux into the sample as the track would overheat and damage the substrate or disintegrate by cracking due to unmatched CTEs.

The green reflector is somewhat indifferent, as it combines the fast initial drop of the blue reflector, but also covered parts of the red spectrum, which may explain the late failures beyond 20 seconds of exposure.

In summary, a blue spectrum exhibited the optimal setting, as high amounts of energy are coupled into the nanoparticles and trigger sintering. The ever increasing absorption cross-section in the blue spectrum, however, may force a thermal runaway effect.

Considering these findings, the PET sample from Figure 5 was revisited. Instead of using reflectors below the sample, the spectral characteristics were now tailored by placing different stacks of blue-absorbing PI below the PET substrate and a white substrate holder during sintering. The sintering settings were equivalent to those used for the samples in Figure 5.

Figure 7 shows the results of the experiment starting with a fresh deposit (a) and a sample processed using a white reflector (b), resembling the characteristics discussed, i.e. no or inconsistent electrical conduction, ragged tracks and condensation of solvent on either side of the track. As layers of 25 µm thick PI foil material were added beneath the PET, the track topology changed visibly and the condensation pattern started to vanish, until it was fully absent with a 4-fold layer of polyimide (cf. Figure 7 (f)). Not only the visual impression of the sintered deposit drastically improved but also electrical conduction paths were virtually absent for Figure 7 (b) and (c) but appeared steady across the 10 mm conductor tracks under consideration in the samples (d) through (f). This was clearly in line with the previously given explanation. While the foil stack on the backside of the PET acted as an absorber for the blue portion of the spectrum provided by the Xenon lamp, it dissipated some of the power into heat which indirectly assisted slight heating of the PET substrate in order to oppress condensation and improve track conformation, while the reduced amount of blue light suppressed the thermal runaway with increasing particle size, allowing for conformal contraction as well as the formation of a continuous conduction path.

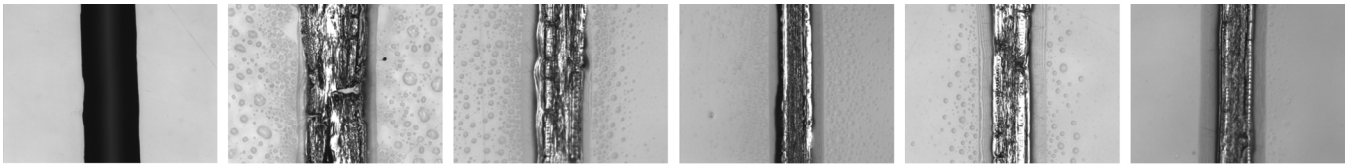
Sintering Via Connections to Bare LED Dies

As in previous publications [9], through-hole connections can be achieved by filling an appropriate via volume using inkjet technology. Here we apply our findings on wet photonic sintering to RMPD®-produced substrates with inlaid bare dies.

The printing was conducted at 70 ºC in order to compensate for the yet non-optimized surface energy of the substrates. Alignment was performed with an accuracy of approximately 25 µm using a DinoLite digital microscope attached to the printhead holder. Connections were printed using 3 layers for the actual connectors and two additional patterns to account for the additional volume necessary in the vias due to their fluctuating volume between 160 and 290 pL.

Sintering was conducted at the optimum settings described in the previous sections. Samples were exposed to 350 J flashes with a repetition frequency of 4 Hz. The length of the exposure was found to be optimal at 6 seconds, resulting in the 24 flashes.

Figure 8 shows the result of the development, where a series connection of 3 LEDs was established. The result was achieved using the afore mentioned absorption approach to guide the heating effect during processing. Previous attempts to sinter with a purely white background resulted in disrupted electrical connections on the top surface of the RMPD® or at the inlet of the



(a) Fresh *(b) Blank* *(c) 1x PI* *(d) 2x PI* *(e) 3x PI* *(e) 4x PI*

Figure 7: Influence of the absorption characteristics of substrate holder on wet sintering of 4 px wide silver lines on PET [flash energy 350 J, pulse width 0.58 ms, repetition rate 4 Hz, sintering duration 6 s]

via, which posed a critical point as the temperature gradient due to the large via volume as well as the geometrical constriction were extreme at this location. The figure shows the LEDs driven just above the threshold at 8.5 V with less than 10 mA of current to omit CCD flooding at higher drive voltages. The configuration was successfully operated at 9.5 V and 20 mA with a series resistor of 120 Ohms to provide sufficient current.

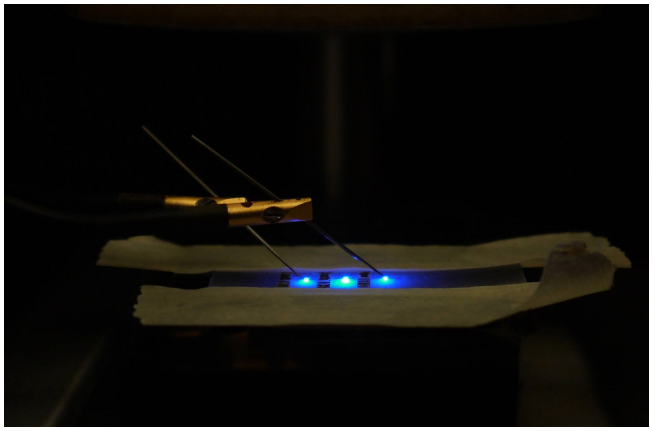


Figure 8: Series connection of three LED performed by inkjet printing with subsequent wet sintering with a driving voltage of 8.5 V at a current of <10 mA [70 ºC substrate temperature, flash energy 350 J, pulse width 0.58 ms, repetition rate 4 Hz, sintering duration 6 s]

Conclusion

In this paper the applicability of broadband photonic flash sintering for wet deposits on non-absorbing substrates has been studied. In conclusion wet photonic sintering was possible, however, only if the process conditions were carefully tuned for the materials under consideration.

The investigated system showed fluctuations in the exposure intensity across the reflector width, which is undesirable for R2R processing, as the intensity maxima pose the boundary conditions for the process in order to suppress superheating of the deposit as well as guarantee a homogeneous illumination of the sample.

Wet sintering was shown to gain resistances of < 5 Ω/cm in < 10 s when taking a minimum energy flux towards the sample into account. The underlying substrate was shown to have an important effect, as upon heating strong temperature gradients force the solute to move and wetting/de-wetting characteristics of the substrate trigger necking of the deposit and subsequent disintegration.

The spectral distribution of the light showed an extensive influence on the course and success of the sintering. It was found that a broadband spectrum seemed not to be very favorable, as diffuse light resonating in the working chamber changed heating characteristics in a negative fashion. It was proven that filtering the blue part of the spectrum at the bottom of the substrate improved track conformation as well as longtime exposure effects even on PET substrates with resistance values of 3 – 4 Ω/cm. These findings suggest to reconsider the design of photonic sintering systems for silver nanoparticles in order to suppress or filter the component of emitted light that triggers excessive heating when approaching grain sizes of >100 nm. A potential design using a laterally tailored blue absorber is depicted in Figure 9. Here sintering characteristics to suppress re-condensation of the evaporated solvent as well as reproducible conductivity achievement can be adapted in space and time irrespective of the illumination system.

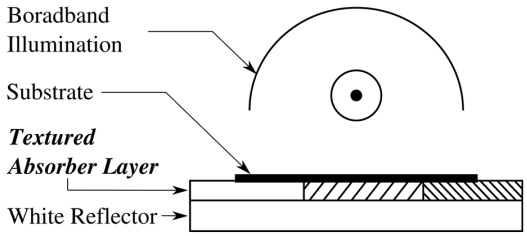


Figure 9: Proposed design for a photonic sintering system employing background spectral tailoring of radiation for optimal wet sintering of inkjet printed silver tracks

Ultimately, our findings were applied to LED via interconnects with via volumes ranging between 160 and 290 pL. The structures were sintered using a blue-absorbing background, yielding triple series connections which could be driven using 9.5 V and 20 mA.

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References

[1] R. Bollström, A. Määttänen, D. Tobjörk, P. Ihalainen, N. Kaihovirta, R. Österbacka, J. Peltonen, and M. Toivakka, Organic Electronics 10 (2010).

[2] W. Zapka et al., "Chemical Post-Treatment of Inkjet Printed Nano-Particle Silver Inks", Proc. NIP 24 (IS&T, Pittsburgh, PA, 2008).

[3] S. Magdassi et al., "Triggering the sintering of silver nanoparticles at room temperature", ACS Nano, 4 (2010), 1943-1948.

[4] A. Schuppert et al., “Ink Jet Printing of Conductive Silver Tracks from Nanoparticle Inks on Mesoporous Substrates”, Proc. DF 27 (IS&T, Minneapolis, MN, 2011).
[5] P. Teunissen et al., “Photonic Flash Sintering of Printed Conductive Structures for Large-Area OLED displays”, SID Spring Meeting 2012, (Stockholm, 2012).
[6] W. Voit et al., “Inkjet Printing of Phase-Change Materials”, Proc. NIP 24 (IS&T, Pittsburgh, PA, 2008).
[7] M.D. Abramoff et al.,”Image Processing with ImageJ”, Biophotonics International 11 (7), (2004).
[8] K. L. Kelly et al., “The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment”, J. Phys. Chem. B, 107 (3), (2003).
[9] I. Reinhold et al., “Inkjet Printing of Electrical Connections in Electronic Packaging”, Proc. DF 27 (IS&T, Minneapolis, MN, 2011).

Author Biography

Ingo Reinhold graduated in micromechanics-mechatronics with emphasis on print- and media technology from Chemnitz University of Technology in 2008. After joining Xaar's Advanced Application Technology group in Järfälla, Sweden, he focused on advanced acoustic driving of piezo-type inkjet printheads alongside with pre- and post-processing of functional materials in digital fabrication. He is currently enrolled as a PhD student within the iPack VINN Excellence Center at the Royal Institute of Technology (KTH) in Stockholm, Sweden.