Novel Developments in Photonic Sintering of Inkjet Printed Functional Inks

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Abstract

Inkjet printing of electrical tracks in roll-to-roll applications was hampered for a long time since nano-particle inks required thermal sintering at temperatures greater than 120 °C for several minutes. Among a large number of potential R2R compatible techniques, photonic sintering of inkjet-printed metal-based inks was shown to enable very fast sintering times and providing high quality of structural integrity and low electrical resistance [1]. While the above investigations were carried out with a low duty-low frequency irradiation source, novel developments allow for pulse shaping on the timescale of several microseconds and, therefore, the combination of drying and sintering pulses into a single piece of equipment.

In this contribution the photonic sintering process was investigated numerically and experimentally for the case of inkjet-printed aqueous copper oxide ink and a Pulse Forge®3200 X2 tool, both implemented onto a NovaCentrix roll-to-roll machine. Our finding support the assumption, that pulse shaping and, therefore, energy tailoring as a function of time, is essential for efficient conversion of wet copper oxide deposits into conductive copper with no impact on the underlying substrate. The paper presents and discusses the resulting electrical resistances of features processed with a conventional hybrid solution using IR-radiation for pre-drying as well as a single step drying and sintering using a single radiation source.

Introduction

Inkjet-printed conductive tracks could be essential features of a large number of printed electronic devices. Key to those printed electronic devices is the possibility to produce them in low cost fashion, which typically requires roll-to-roll manufacturing techniques and cheap substrates. A problem to be solved is the post-treatment that is required to dry and to sinter the inkjet-printed nanometallic particle inks. This post process has to be carried out in a fast fashion to allow roll-to-roll manufacturing and to be conducted with such low thermal impact that does not induce damage to the substrate.

Photonic sintering is the high-temperature thermal processing of a thin film using pulsed light from a flashlamp [2]. When this transient processing is done on low-temperature substrates such as plastic or paper, it is possible to attain a significantly higher temperature than the substrate can ordinarily withstand under an equilibrium heating source such as an oven. Since the rate of most thermal sintering processes (drying, sintering, reacting, annealing, etc.) generally increase exponentially with temperature (i.e. they obey the Arrhenius equation), this process allows materials to be cured much more rapidly (in about 1 millisecond) than with an oven taking usually several minutes. Photonic sintering not only allows a dramatic increase in the processing speed, but it also enables the creation of new materials not possible with an ordinary oven as certain limitations of equilibrium thermal processing are eliminated. Photonic sintering was demonstrated earlier as a viable technique for fast sintering of silver nanoparticle inks with no damage to polycarbonate substrates [4].

Of advantage due to lower material cost is the usage of copper inks for inkjet printing of conducting tracks. However, due to the considerably higher temperatures required for sintering of copper oxide particles, the development of a fast sintering process on thermally sensitive substrates is specifically challenging. In this paper, an advanced variant of photonic sintering is used in which a chemical reaction between copper oxide and a reducer is modulated by the beam from the flashlamp to form a mesoporous copper film.

Experimental

A commercial ink, Metalon® ICI-002HV (NovaCentrix, US), containing 16 wt% nanosized copper oxide particles (130-140 nm) and reducing agents was used throughout the experiments. The viscosity of this ink was measured using a Rheosense µVISC rheometer and yielded 12 cP. The surface tension was measured using Krüss Easydyne as 24 mNm^{-1}.

Jetting was performed using a standard-type Xaar 1001 GS6 printhead in combination with an industrial Hydra recirculating ink system (Xaar, UK). As the work reported here focuses on the post-processing technique and not primarily on the jetting, potential reduced lifetime of the printhead in combination with aqueous fluids was disregarded.

Printing was carried out on a proprietary print rig, comprising an un- and rewinder (Propheteer, US). Pre-drying was accomplished by an IR dryer (6 kW, DRI, US) with a drying length of 0.5 m. Novele™ (NovaCentrix, US), a coated PET foil, was used as the substrate in all experiments.

A PulseForge®3200 X2 (NovaCentrix, US) was used for drying and sintering. Resistances were measured using a 2-point probe (Fluke, US). Line width was measured using a digital microscope (Quick Vision ELF, Mitutoyo, JP).

Photonic sintering pulse shape optimization was carried out using a commercial FDTD code (SimPulse™, NovaCentrix, US) integrated into the PulseForge tool.

Results and Discussion

A special waveform was created to give 6 ms^{-1} droplet velocity and seven greylevels with the standard Xaar 1001 printhead. Reliable jetting was found up to 4 kHz, which corresponds to a printing speed of 0.25 ms^{-1} at the nominal resolution of 360 dpi in print direction.

Optimized printing conditions were found by using different resolutions in printing direction in order to obtain straight outer contours of line features for consistent resistance values as well as reduced defects during formation, which would yield strong dewetting and following disintegration as discussed in [1]. The line features under consideration were oriented along the printing direction, where the slight deviations originating from the stagger of the fixed-resolution printhead (cf. [3]) could be disregarded and the post-processing technique could be analyzed quantitatively.

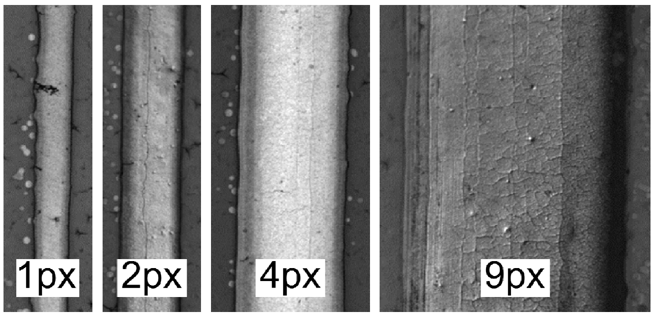

Figure 1: Illustration of the achieved line homogeneity of printed, dried and sintered tracks at a feed rate of 0.12 ms^{-1} [360x540 dpi, ICI-002HV on Novele™ substrate]

Good line formation with sufficient coverage of the substrate was found for a resolution of 540×360 dpi using a nominal droplet volume of 42 pL, which gives a liquid volume of 19 nL mm^{-2}. Figure 1 shows the achieved line morphologies with the printing parameters given above. The outline of the achieved features was very homogeneous and did not show signs of dewetting. An interesting feature visible in all lines printed with more than a single pixel is the resemblance of the individual trace of the nozzles in the dried and sintered pattern. This may be attributed to the swift absorption of the solvent into the particulate topcoating of the used substrate. In this fashion, the time delayed deposition from neighboring nozzles due to the intrinsic resolution of the printhead generated these layered deposits. When surpassing a threshold, where the topcoating became saturated, the final structure was more homogeneous as shown in the 9 px line. Here one could observe a shallow single line deposit on the left hand side of the track, while the morphology towards the right hand side appeared more like a 2.5d structure with a characteristic coffee ring. As the coating could no longer take up more solvent, a liquid track was produced, which allowed for the flow of particles to its outer rim and generate the typical structure.

Figure 2 depicts the line gain, where a linear relationship was found. This again reflected the good absorption properties of the substrate coating and the resulting pinning of the line width by the quick removal of a large portion of the solvent. The linear regression resulted in an increase of about 63 µm per added pixel, instead of the expected 70.5 µm for the resolution of the printhead.

Sintering Optimization

Two different approaches were pursued in this investigation in order to verify the capability of R2R processing using impulse light processing. A first approach mimicked the classical hybrid

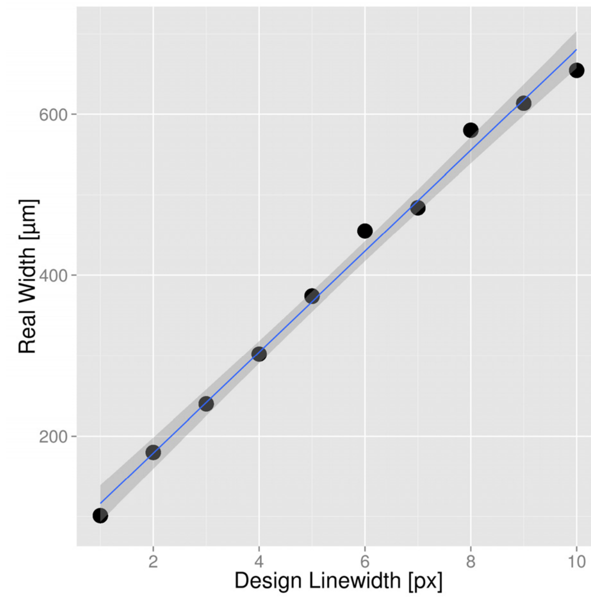

Figure 2: Comparison of the designed and achieved width of printed, dried and sintered tracks at a feed rate of 0.12 ms^{-1} [360x540 dpi, ICI-002HV on Novele™ substrate]

approach, where a pre-drying step was carried out using external drying equipment, which may be low-energy impulse light, IR radiation, etc. Thereby, solvent was driven out of the fresh, wet deposit and allowed for processing with high energy light pulses (in the following referred to as "uniform"), to selectively heat up the nanoparticles without superheating the solvent and *blow off* of the deposit. Alternatively, pulse-shaping utilizing a train of pulses with different durations as well as amplitudes (referred to as "pulse-shaped") was applied in such a fashion, that during the initial phase of the illumination moderate temperatures were generated in order to drive off the solvent. Following this stage the typically applied high energetic illumination triggered the chemical conversion of copper oxide to pure copper.

Figure 3 shows the average values of the resistance found. The pulse settings for the uniform pulses varied in combinations of voltage between 340 and 420 V, number of sub-pulses between three and twelve as well as a variation of the overlap factor of pulses on the substrate between four and ten. For low feed rates a minimum drying power of 60% was necessary in order to sinter the deposit without *blow off* of the deposit. With optimal settings this resulted in resistances down to 9.5 Ω/cm for a 4 pixel wide line.

As the web speed increased, higher drying power was necessary, as the remainder of the liquid carrier led to local overheating and explosive disintegration or even full *blow off* of the printed tracks. As can be seen from the graph, only higher pre-drying with up to 100% drying power was able to achieve similar results for the 0.12 ms^{-1} feed rate. An additional increase to 0.18 ms^{-1} left only 100% as the choice for pre-drying, as all other settings showed insufficient or inconsistent sintering. Here sintering could not yield the resistances lower than 19 Ω/cm.

Utilizing the arbitrary pulse showed clearly superior performance. The pulse in this case is designed using SimPulse™ and gave theoretical surface temperature of the deposit of

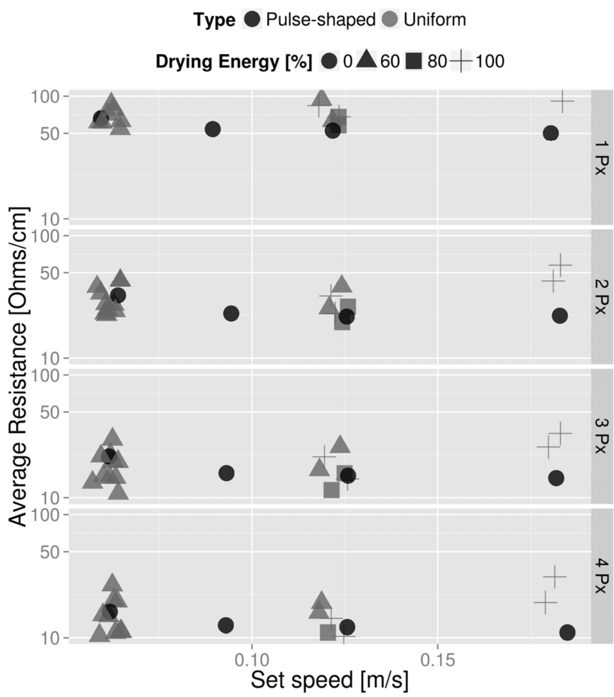

Figure 3: Resistance of the inline printed, dried and sintered structures as a function of IR drying power, pulse shape, set line speed and line width. [360x540 dpi, ICI-002HV on Novele™ substrate, jitter was added to the set speed in order to prevent overplotting].

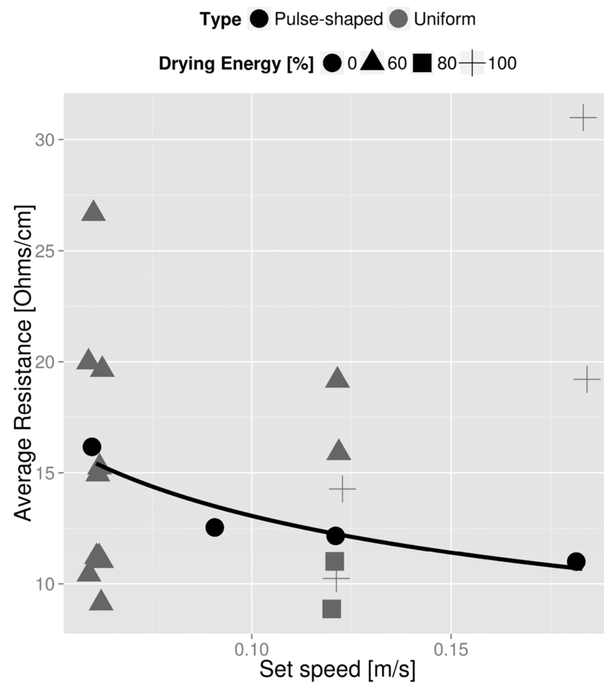

Figure 4: Average resistance of the inline printed, dried and sintered structures as a function of IR drying power, pulse shape, set line speed for a four pixel wide line. The solid line represents a power fit of the data points from the experiments using the arbitrary pulse[360x540 dpi, ICI-002HV on Novele™ substrate, jitter was added to the set speed in order to prevent overplotting].

approximately 300 °C for pre-drying followed by a sintering pulse with 700 °C. The calculated numbers were only an estimate for the actual temperatures as the simulation in its current state did not consider phase transitions. As depicted in Figure 3, slightly higher resistances could be achieved for the lowest feedrate, however, without the need for pre-drying. As the feedrates increased, constant or even improved resistance values were found. Figure 4 shows the data for the 4 pixel wide lines with a power fit of the results for the arbitrary pulse, yielding 11.5 Ω/cm. One possible explanation for the decrease of the resistance with increasing feedrate could be the thermal energy building up in the chuck supporting the substrate underneath the flashlamp. As more pulses are triggered from the internal encoder per time unit, the equilibrium temperature of the support may have reached a considerable level to assist drive off of the solvent and improve the result. Figure 4 furthermore shows that the hybrid process appears more optimal at lower feed rates, which may reflect the time scales of heating the liquid carrier of the ink and the associated dynamics while the deposit was still in its liquid state. Therefore, with a trade-off in machine space and processing time, a more optimal solution may be achieved using the hybrid approach.

Conclusion and Outlook

The presented experiments show the applicability of the PulseForge® technology to wet photonic sintering of inkjet-printed copper ink. Using pulse shaping, which allowed for the modulation of the applied energy through amplitude and duration changes on a microsecond timescale, pre-drying and sintering could be accomplished using a single lamp in a R2R machine. While the electrical performance was suboptimal compared to the hybrid sintering approach using IR-drying and photonic sintering at lower feedrates, the results strongly improved at higher feed rates without the limitation of pre-drying.

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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.