Combined Sintering Approaches for Fast Sintering of Inkjet Printed Nanoparticles for R2R Applications

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Abstract

Inkjet printing is a nascent technology that developed during the last decades from only printing text and graphics into an important scientific research tool for R&D, where printers are used as a highly reproducible non-contact patterning tool. In contrast to lithography, inkjet printing is an additive technique that requires only small amounts of functional materials and, therefore, has a high materials efficiency. In particular, inkjet printing of metal nanoparticle dispersion has been used more and more during the last few years, in order to produce conductive features for plastic electronic applications.

Here, we present our recent results in the sintering of inkjet printed metal nanoparticles on polymer foils. In order to sinter the particles at speeds that are compatible with roll-to-roll speeds, we have used a combination of sintering methods. Conductivity values between 40 and 60% were obtained in a few seconds to minutes by using either photonic or plasma pre-sintering combined with microwave flash sintering.

Introduction

Inkjet printing of conductive precursor materials – usually metallic nanoparticles or metal organic complexes – has been used as a relatively fast technique that might enable roll-2-roll (R2R) production.[1-3] However, the sintering step that is necessary to render the precursor compounds conductive typically requires >30 minutes and/or higher temperatures (>250 °C). In particular, the long sintering time is not scalable to R2R production lines and the high sintering temperatures are not compatible with paper or common polymer foils that have a relatively low glass transition temperature (Tg). Both the temperature and the time required for sintering clearly need to be reduced and this has, therefore, been the research for many scientists over the last few years.[1-5]

Inkjet printing of metal precursor inks has been used for many applications, such as interconnections for a circuitry on a printed circuit board,[6] disposable displays and radio frequency identification (RFID) tags,[7] organic thin-film transistors,[8] and electrochromic devices.[9] Despite the many successes in the inkjet printing of metal precursor inks as a rapid fabrication tool for plastic electronic applications, some challenges still remain.

Firstly, the processing temperature needs to be below the Tg of the substrate materials and the decomposition temperature of protecting materials, such as barriers or insulating materials. Secondly, the current resolution of inkjet printing is in the order of micrometers and, therefore, cannot be compared with the resolution of lithographic techniques, including soft-, photo- and nano-imprint lithography, that have a nanometer resolution.[10] The current industrial state of the art feature size of 32 nm has been achieved as a consequence of an enormous financial and intellectual effort, over the last 60 years. While this technology is needed for state of the art high frequency circuits, the appeal of inkjet printing comes into play when the focus is placed on properties other than speed or feature density. The great advantage of inkjet printing is that it is a 'mask-less' process; it can quickly switch from one design to another without the need for a new set of expensive masks, which enables a much more flexible processing flow.[11] It is also not limited to a few rigid substrates, like silicon or gallium arsenide. Therefore, a trade-off exists between resolution and flexibility.

Finally, conductivity values need to reach a certain application dependant value. Typically, the obtained conductivity after the sintering step is only a fraction of the bulk metal conductivity. The conversion of the precursor ink into bulk material is affected by the processing temperatures, which are well below the melting temperature of bulk metal. This can be compensated for by printing multiple layers,[12] which comes at the cost of more needed material and time. Therefore, another trade-off appears between the processing conditions and the feature's conductivity.

Here, we summarize alternative and selective sintering methods that can sinter as-printed metal nanoparticles below the Tg of common polymer foils. Furthermore, we present the sintering of metal nanoparticles at speeds that are compatible with R2R production. By a combination of plasma or photonic pre-sintering, followed by a microwave flash sintering step, conductivities up to 60% were revealed in short times

Sintering approached for nanoparticle inks

After a metal-containing precursor ink has been deposited onto a substrate, an additional processing step is required to render the as-printed patterns conductive: a process called *sintering*. In the case of a heating a nanoparticle ink, the nanoparticles lose their organic shell and start showing conductance by direct physical contact. Conductivity only arises when metallic contact between the particles is present and a continuous percolating network is formed throughout the printed feature. An organic layer between the silver particles as thin as a few nanometers is sufficient to prevent electrons moving from one particle to another.[13] When metal nanoparticles are created, larger particles will form through

Ostwald ripening;[14] a process whereby the surface energy is reduced due to the particles' large surface-to-volume ratio.

The conversion of non-conductive precursor inks has been reported mostly by simply applying heat. However, typical sintering temperatures are above 200 °C,[13] which is not suitable for common polymer substrates that have a relatively low glass transition temperature (Tg), like polyethylene naphthalene (PEN) and polyethylene.[3] In fact, only the expensive high-performance polymers, like polyimide and polytetrafluoroethylene can be used at high temperatures, which represent a drawback for implementation in large area production and are not favorable in terms of costs.

A first selective sintering technique, which was developed by Reinhold *et al.*, is to expose the printed features to a low pressure argon plasma.[15] This process decomposes the organic moieties around the nanoparticles within the printed feature from top to bottom, which can be followed by a growing skin layer in time. After a sufficient amount of sintering time, the as-printed features are converted into *bulk* material. The authors confirmed the skin layer formation by applying adhesive tape to the partially sintered printed structures, which removes the conductive top layer, while leaving the designated unsintered part of the material behind. Removing the upper layer revealed a characteristic bluish appearance of nanoparticles, which did not show conductivity. The crust that was transferred to the adhesive tape, however, was conductive and showed similar resistance compared to the complete track before. Subsequent plasma processing of the sample yielded again conductivity (see Figure 1).

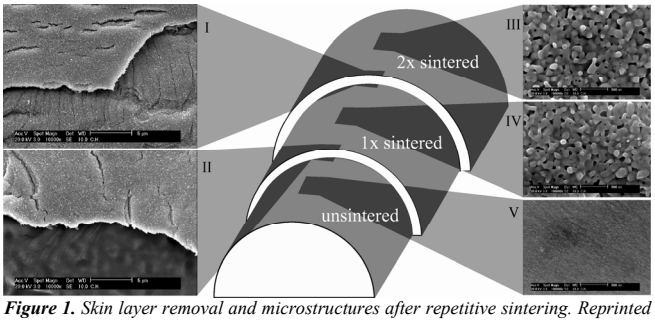

Figure 1. *Skin layer removal and microstructures after repetitive sintering. Reprinted from ref. [15].*

A second example of selective sintering is by using microwave radiation.[16] Typically, highly conductive materials, *e.g.* metals, have a penetration depth of 1 to 2 µm at a microwave frequency of 2.45 GHz. It is believed that the conductive particle interaction with microwave radiation, *i.e.* inductive coupling, is mainly based on Maxwell-Wagner polarisation, which results from the accumulation of charge at the materials interfaces, electric conduction, and eddy currents.[17] In contrast to the relatively strong microwave absorption by the conductive particles, the polarisation of dipoles in thermoplastic polymers below Tg is limited, which makes the polymer foil's skin depth almost infinite, hence transparent, to microwave radiation. Exposing metallic nanoparticles to microwaves does not only reveal a sintering process taking place, but also the sintering time is hereby decreased by a factor of 20, while conductivity values are similar when using thermal sintering. By the application of conductive antenna structures around features that exhibit a small conductance, the exposure times could be reduced to only a single second, as described by Perelaer *et al.*, recently.[18] In fact, the antenna structures do not require a physical contact with the unsintered features, which makes recycling of the antennae possible. This process can then be implemented into roll-to-toll (R2R) production. After sintering the features revealed a conductivity of up to 34% when compared to the bulk silver value.

As a final example, photonic sintering is listed here, which uses a high intensity white light beam to sinter metal precursor inks (see Figure 2). This relatively new technique is, for example, commercialized by NovaCentrix.[19] The tool produces very short pulses of white light with a maximum of 100 kW cm^{-2} to deliver the energy to the target material. By careful control of the duty cycle of the lamps, the energy delivery to the inks can be stopped at the right moment, *i.e.* just before enough energy is delivered to convert the ink into its conductive form and to prevent substrate damage. Conductivity values of 25 to 30% of bulk metal were obtained with translational speeds of up to 100 meters per minute.

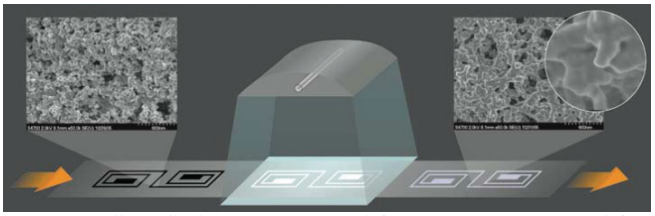

Figure 2. *Roll-to-roll photonic sintering tool from NovaCentrix. Reprinted from PulseForge™ brochure, http://www.novacentrix.com.*

Other techniques that are reported in the open literature and have been used for sintering include exposure to UV radiation,[20] electric sintering,[21] and LASER sintering.[22]

Recently, Magdassi *et al.* discovered that silver nanoparticles behave as soft particles when they come into contact with oppositely charged polyelectrolytes and undergo a spontaneous coalescence process at room temperature.[23] Triggered by these findings, the authors have inkjet printed a solution containing the cationic polymer poly(diallyldimethylammoniumchloride) onto an as-printed film of silver nanoparticles that are stabilized by poly(acrylic acid), which lead to the sintering of silver nanoparticles and the formation of conductive films without further heating. The obtained conductivity was approximately 20% compared to bulk silver.

Combined alternative sintering methods

In order to obtain sintering speeds that are compatible with R2R production, a combination of two alternative sintering techniques was used here. Thermal sintering could not be used, since the polymer substrates have a Tg lower than the required sintering temperature of the metal nanoparticles – the latter one being more than 150 °C.

Figure 3 shows a schematic representation of a sample with four silver electrode/antennae structures, which increase the absorption of the microwaves,[18] and on top a single silver line.

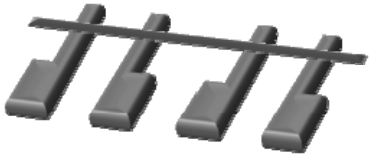

Figure 3. *Schematic representation of the printed template with four silver electrodes/antennae and a single silver line inkjet printed on top of the antennae. The total length of the line is 1.6 cm.*

After inkjet printing a single line over the antenna structures, a pre-sintering step was performed by using photonic sintering. Figure 4 depicts a scanning electron microscopy (SEM) image of inkjet printed silver nanoparticles (Suntronic U5603) after photonic pre-sintering. It can be seen that the nanoparticles have merged into larger agglomerates due to sintering and that, subsequently, a continuous network for electrons has been created, hence becomes conductive. At this point the conductivity was approximately 20% of bulk silver.

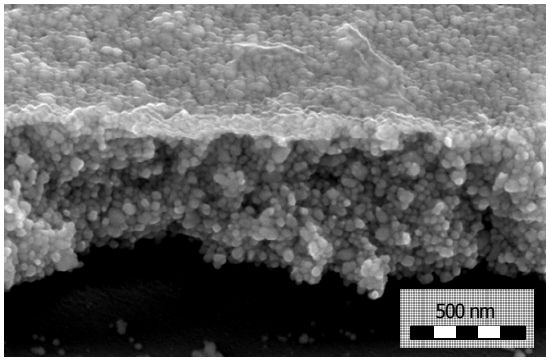

Figure 4. *Scanning electron microscopy (SEM) image of inkjet printed silver nanoparticles on PEN substrate after photonic flash pre-sintering.*

In order to further sintering, hence increase the conductivity, microwave flash sintering was used subsequently. Figure 5 shows an SEM image of the same track after microwave flash sintering. Due to the microwave exposure, the nanoparticles have sintered further and the conductivity increased to approximately 40%.

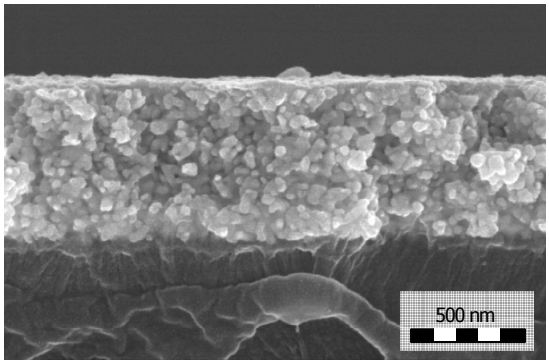

Figure 5. *Scaning microscopy image of inkjet printed silver nanoparticles after photonic flash pre-sintering, followed by microwave flash sintering.*

Furthermore, we have used a tailored silver nanoparticle ink with a similar combined sintering approach. The customized silver ink was made in such a way that the organic stabilizers around the nanoparticles provide sufficient stability to inkjet print the ink, but the organics are also weakly enough bound to the particles that they can be removed at a low temperature. By using plasma pre-sintering followed by microwave flash sintering, conductive silver features were obtained with a conductivity up to 60% that of bulk silver.

Conclusions

In conclusion, we presented a method to sinter as-printed silver nanoaparticles in times that are compatible with roll-to-roll production speeds and common polymer substrates that have a relatively low Tg. By combining photonic pre-sintering with microwave flash sintering, conductivities of 40% of bulk silver were obtained in only a few seconds. When using a tailored silver nanoparticle ink and the combination of plasma and microwave flash sintering, conductivity values up to 60% were obtained in a few minutes.

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