Low Temperature Sintering of Inkjet Printed Metal Precursor Inks for Organic Electronic Applications

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Abstract

As a nascent technology that developed during the last decades from only printing text and graphics into an important scientific research tool for R&D, inkjet printers are nowadays used as a highly reproducible non-contact patterning tool. In contrast to non-digital patterning tools, inkjet printing represents an additive technique that requires only small amounts of functional materials and is therefore characterized as being a highly efficient materials patterning technique. In particular, inkjet printing of metal precursor materials 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 nanoparticle dispersion on cost-effective polymer foils. In order to sinter the particles at speeds that are compatible with roll-to-roll speeds, we have used combinations of innovative sintering methods. Conductivity values between 40 and 60% were hereby obtained in a few seconds to minutes by using either photonic or plasma pre-sintering followed by microwave flash sintering.

Introduction

Within the last decade, inkjet printing technology has developed from only a text and graphic industry to a major topic of scientific research and R&D. Inkjet printing can be used as a flexible, non-contact and digital patterning technique to print at high speeds either small or large areas with high quality features; it requires only small amounts of functional materials, which enables a simple form of processing as well as a cost-effective production.[1-3] Furthermore, inkjet printing reduces the amount of processing steps due to its additive technique of materials deposition, which further decreases productions costs.

In the last years, inkjet printing of inorganic nanoparticles has gained an increased interest, because of the possible applications as contacts and interconnects in radio frequency identification (RFID) tags, organic light emitting diodes (OLED) and organic photovoltaics (OPV).[4,5] The main challenges of using inorganic nanoparticles, for example silver, as precursor materials are a low conversion temperature (<150 °C) that is compatible with common polymer foils as well as a fast conversion time that enables roll-to-roll (R2R) processing. Promising alternative sintering techniques include plasma,[6] photonic[7] and microwave flash sintering.[8] Furthermore, more cost-efficient materials should be chosen, such as copper or aluminum,[9] as the price for silver is continuously increasing. Such materials, however, require a protective atmosphere, as oxidation may take place under ambient conditions, which complicates the process and increases the manufacturing costs.

In this contribution, an overview of our latest results on the low temperature conversion of inkjet printed metal nanoparticle dispersions on cost-effective polymer foils in short processing times is given. A variety as well as a combination of innovative sintering tools were used, including photonic, plasma and microwave flash sintering in order to sinter at R2R speed.

New, alternative and innovative sintering approaches

Once a metal nanoparticle ink is deposited on a substrate, an additional processing step is required to render the as-printed patterns conductive.[3] This process can be divided in two stages, whereby at first, the organic coating is removed from the metal nanoparticle at the curing temperature. At this stage the metal particles make direct physical contact and have a relatively low conductance.[10] In the second stage, larger particles will be formed at the expense of smaller particles due to grain growth, sintering and *Ostwald ripening*. Driven by the size difference between particles, the process of Ostwald ripening stalls when a particle diameter of approximately one and a half times their original size is reached, leaving behind a porous structure, and lower conductivity values than the bulk material are obtained.[11] The transport of material between particles during Ostwald ripening is non-convective and purely of a diffusive nature. Due to the large surface-to-volume ratio of small particles, a reduction of surface energy, *i.e.* sintering, will take place, followed by a mass flow to increase the neck radii and larger particles will form.

Generally, there are two approaches to enable low temperature sintering of inkjet printed metal nanoparticle inks. The first approach is to tailor the ink in such a way that the protective capping agent of the metal nanoparticles can be removed at a low temperature. Researchers have explored this possibility successfully by using low amounts of organic additives, which enabled a sintering temperature of 80 °C.[3] One step further, Magdassi *et al.* found 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.[12] Triggered by these findings, the authors have inkjet printed a solution containing the cationic polymer poly(diallyldimethylammoniumchloride) (PDAC) onto an as-printed film of silver nanoparticles that are stabilized by poly(acrylic acid) sodium salt (PAA), which lead to the sintering of silver nanoparticles and the formation of conductive films without further heating, as depicted in Figure 1. The obtained conductivity was approximately 20% of bulk silver. The authors believe that the positively charged polymer PDAC removes the charge stabilization that was obtained by the negatively charged PAA stabilizing agent. It was shown that for a PDAC/Ag ratio of 0.12 the zeta-potential reached a zero value and precipitation of aggregated NPs occurred. The original NP ink had a zeta-potential of -47 mV.

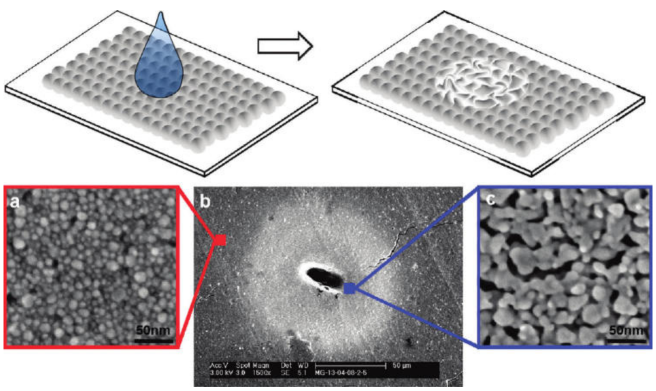

Figure 1. Top: Schematic illustration showing what happens when a droplet of PDAC solution is printed onto a silver NPs array. Bottom: scanning electron microscopy (SEM) image of a printed drop zone (b) and the magnified images of NP arrays after the contact with PDAC outside (a) and inside (c) the droplet zone. Reprinted from reference 12.

Secondly, alternative energy sources are used to selectively expose the as-printed nanoparticles. The common method of sintering is by heating the structures to a temperature >150 °C, which is not compatible with commonly used polymer foils that have a low glass transition temperature, such as polyethylene therephthalate (PET) and polyethylene naphthalate (PEN). By using other energy sources, such as microwave[13] or intense pulsed light,[14] only the as-printed metal precursor structures are heated and only for a short time, which prevents (permanent) damage to the underlying substrate. However, longer sintering times may damage the substrate, as it will heat due to contact heating by the sintered features. By carefully tuning the frequency as well as the energy, a successful sintering can be revealed without damaging the substrate.

In the following paragraphs, a variety of examples of selective post-printing processed are discussed to convert the metal precursor ink into conductive materials. The crucial point here is the fast as well as efficient sintering of the materials, while keeping the underlying polymer substrate unaffected.

In 2006, it was shown that microwave radiation can be used as an alternative and selective sintering technique for inkjet printed silver nanoparticles.[13] Typically, the conductive materials 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 polarization, which results from the accumulation of charge at the materials interfaces, electric conduction, and eddy currents. Due to the strong absorption of microwaves by the conductive structures, the polymer substrate is not heated and remains unharmed. 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 to those obtained by thermal sintering.

A further reduction of the sintering time was realized by the application of conductive antenna structures around the features that will be sintered (Figure 2). Hereby, the microwave exposure times were reduced from three minutes to only a single second. This process is referred to as microwave flash sintering. A low initial conductivity of the features is required, which subsequently triggers the microwave radiation more efficiently. The pre-sintering can be done either by thermal sintering[8] or by using photonic sintering.[7] The latter sintering technique is preferred for pre-sintering as it introduces less thermal stress to the polymer foil.[15]

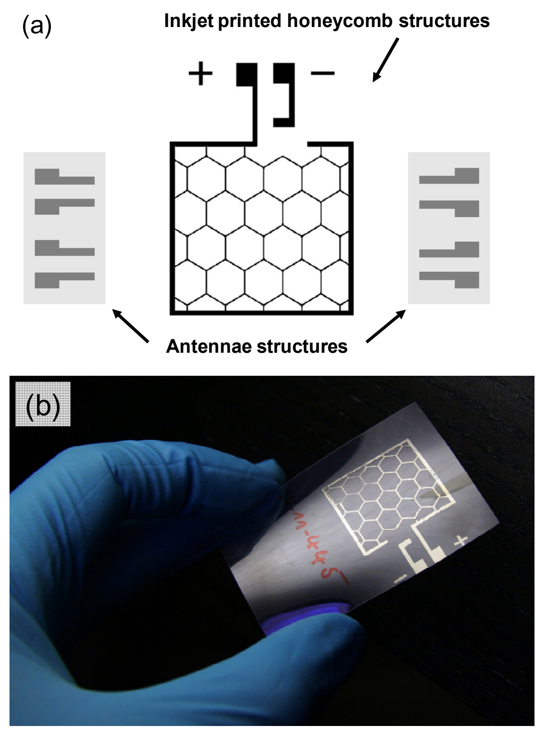

***Figure 2**. Schematic representation of the printed template (a), with four silver antennae in gray (left and right) surrounding a honeycomb structure (middle). Not drawn to scale. Inkjet printed honeycomb structure after photonic sintering and subsequent microwave flash sintering (**b**). Reprinted from reference 7.*

Recently, we used the combination of an alternative sintering approach and a tailored silver nanoparticles ink.[16] The as-printed silver nanoparticle formulation was then sintered by using a two-step procedure: at first, a low-pressure argon plasma exposure, which resulted in a low conductivity of at least 0.1% of bulk silver. It was found that the resistivity development stabilizes after 20 minutes and reaches a plateau value at approximately 2.8×10^{-7} Ω.m, which is approximately 6% of bulk silver.

Complete sintering of the features was then realized by subsequent microwave flash sintering. The conductivity was significantly improved by exposing the features to a microwave source for a single second. Using both sintering techniques in a sequential manner revealed a final conductivity of 60% in less than 10 minutes.

Figure 3 shows scanning electron microscopy (SEM) images of the as-printed silver nanoparticles (top), after plasma pre-sintering for 30 minutes at 150 W (middle) after a microwave flash exposure of 1 second at 1 W (bottom), respectively.

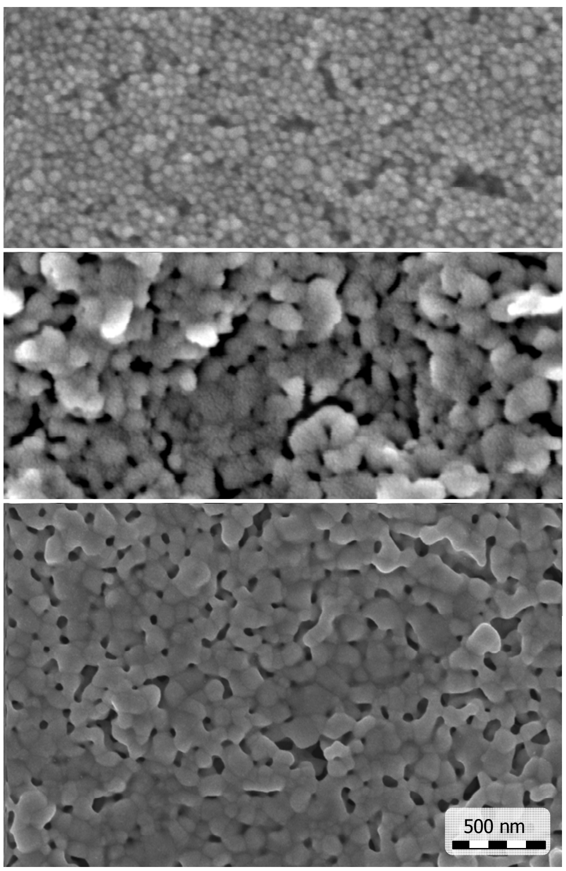

Figure 3. Top view scanning electron microscopy (SEM) images of as-inkjet printed silver nanoparticles (top), after plasma pre-sintering (middle) and after subsequent microwave flash sintering (bottom), respectively. Reprinted from reference 16.

To demonstrate the applicability of such a sintering technique for plastic electronics, a flexible, transparent PET-based electroluminescence (EL) device was constructed (Figure 4). The silver ink was inkjet printed onto a four-layer (PET : ITO : ZnS : $BaTiO_3$) electroluminescence device. Then, the printed EL device was exposed to argon plasma for a period of 3 min. Figure 4 shows the device with an applied voltage (100 V) between the ITO and the silver electrodes, which resulted in light emission corresponding to the silver printed pattern. Moreover, the fabricated EL device showed a good flexibility.

Figure 4. Electroluminescent device prepared by a tailored silver nanoparticle ink and low-pressure plasma sintering. Reprinted from reference 16.

The approach of using an alternative sintering technique combined with a tailored silver nanoparticle ink was also used to prepare ultra-high frequency radio frequency identification (UHF RFID) tags on PET.[4] The rapid low-pressure argon plasma sintering process yielded 11% bulk silver conductivity within one minute and up to 40% for longer sintering times. A photograph of an UHF RFID antenna is shown in Figure 5.

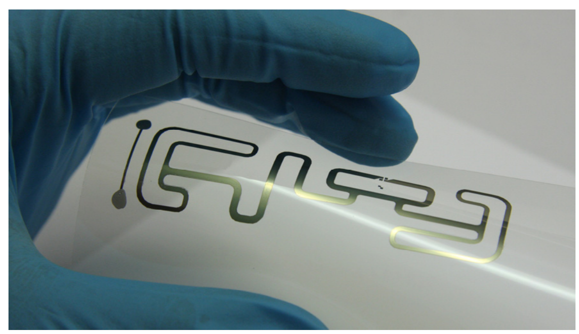

Figure 5. Inkjet printed RFID antenna on PET foil. Reprinted from reference 4.

Finally, a very recent development is the usage of atmospheric pressure plasma exposure for sintering inkjet printed metal nanoparticles (Figure 6).[17] This method was found to be faster and more substrate friendly than low-pressure plasma sintering. In fact, the applied processing times were reduced from more than 30 minutes to 4 seconds for low pressure plasma sintering and atmospheric pressure plasma sintering, respectively, representing a significant acceleration of the state-of-the-art argon plasma sintering. A final conductivity of up to 12% of bulk silver was obtained.

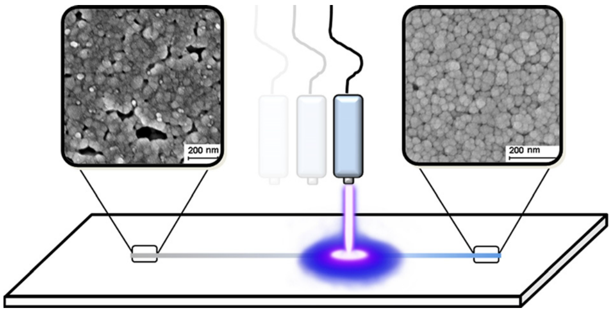

Figure 6. *Schematic representation of the atmospheric pressure plasma sintering process. Reprinted from reference 17.*

Conclusions

Various approaches to sinter inkjet printed metal nanoparticle inks on cost-effective polymer foils were presented here. It was found that a sequential setup of plasma and microwave flash sintering in combination with a tailored nanoparticle ink resulted in conductivity values up to 60% of bulk silver. Whereas photonic pre-sintering followed by microwave flash sintering revealed a conductivity up to 40% in 15 seconds. The obtained conductive features can be used, for instance, as conductive grid structures for OLED and OPV applications, as well as electroluminescent devices and conductive antenna structures for radio frequency identification (RFID) tags.

The presented sintering methods represent a significant step towards roll-to-roll (R2R) production of printed electronic applications, where cost-effective flexible polymer foils and low processing temperatures are required.

Acknowledgement

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Author Biography

Jolke Perelaer obtained his masters in chemistry at the University of Utrecht in the Netherlands in 2004. He finished his PhD within the group of Prof. Schubert (Eindhoven University of Technology, the Netherlands, 2009) with the focus on the preparation of (conductive) microstructures via inkjet printing and embossing techniques. He continued his work with Prof. Schubert as project manager of the inkjet group at the Friedrich-Schiller-University in Jena, Germany. The topics include printed electronics, combinatorial materials screening and printed bio-materials.