

Inkjet Printing and Low Temperature Sintering for Organic Electronic Applications

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Abstract

In recent years, inkjet printing is increasingly used as a flexible and digital patterning technique in order to deposit functional materials for the manufacturing of microelectronic applications,^[1] including radio frequency identification (RFID) tags,^[2] organic photovoltaics (OPV),^[3] organic light emitting diodes (OLED)^[4] and printed circuit boards.^[5] Due to its minimal waste generation and its efficient handling of expensive materials, inkjet printing represents a widely accepted alternative to conventional patterning methods, such as vapor deposition and photolithography.^[6] In terms of the deposition of conductive materials, inkjet printing of metal precursor inks as well as the sintering of these materials after printing is of great interest. In order to apply sintering conditions that are compatible with the thermo-sensitive polymer substrates, we present here a combination of alternative sintering methods, photonic and microwave flash sintering.^[7] Secondly, inkjet printing is used as a tool to deposit light emitting polymer films from solution. We present the investigation of ink properties as well as printing conditions of three polymers (red, blue and green emitting) in order to form homogeneous films with defined thicknesses for application in OLED devices.

Low temperature sintering

In order to manufacture contacts and interconnects, inkjet printing of conductive precursor materials, like metal nanoparticle inks (NP)^[8] and metal organic decomposition (MOD) inks,^[9] has gained significant interest within the last years. Frequently used NP inks are nanoparticles of a size usually smaller than 50 nm in organic solvents or water. The dispersed nanoparticles are stabilized by organic additives to prevent agglomeration and to ensure good processability.^[10-11] As additives, long alkyl chains with a polar head, such as thiols or carboxylic acids, are frequently used.^[11-12] For a cost-effective production of printed electronics, the substrate should be inexpensive as well as available in large quantities to ensure roll-to-roll (R2R) production capabilities. Typically, low-cost polymers have a relatively low glass transition temperature (T_g), i.e. the temperature at which the material starts deforming, which restricts the process to take place at low temperatures. After printing the inks, the metal nanoparticles are still separated by the organic shell, which prevents electron transfer and acts as insulating layer. In order to gain conductivity, the organic material has to be removed from the particles' surface

in order to provide contact of the metal particles. Removal of the organic shell can be obtained by conventional heating above the decomposition temperature of the organic moieties, resulting in direct physical contact to each other and, as a consequence, merging of the particles by the formation of necks,^[1] due to Ostwald Ripening.^[13] This post-printing process is called sintering.

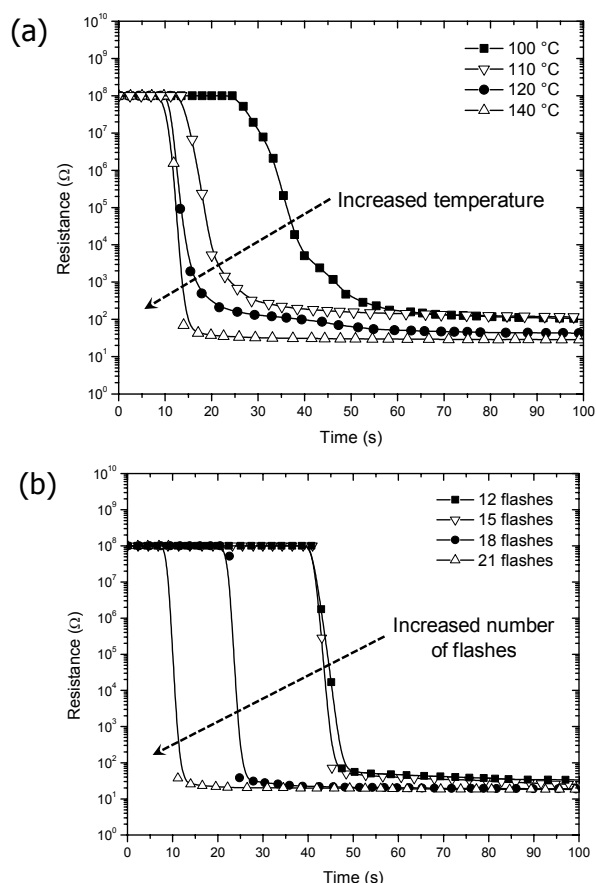


Figure 1. Effect of the temperature (a) and number of flashes for photonic pre-sintering (b) on the final resistance of an inkjet printed silver nanoparticles ink. Reprinted from reference 7.

Sintering temperatures, however, are usually not compatible with commonly used polymer foils that have a glass transition temperature well below 200 °C, such as polycarbonate (PC) or polyethylene terephthalate (PET). Actually, with thermal sintering only high performance polymer foils, like polyimide (PI), can be used. Furthermore, the long sintering times of up to 60 minutes are a major drawback for mass-production processes.

In order to develop a sintering method that is compatible with thermo-sensitive polymer substrates, one of the options is the application of selective sintering techniques, such as focused LASER beam,^[14] a low pressure argon plasma exposure,^[15] microwave radiation^[16] or photonic sintering^[17]. Instead of heating the entire sample, these methods enable a selective heating of the printed structure exclusively, which allows to sinter the metal nanoparticles in a more efficient manner at process conditions that do not harm the substrate material. Furthermore, research is focused on the fast sintering of nanoparticle inks with the aim to enable R2R processing. Techniques that are capable of fast sintering times are, for example, microwave flash sintering^[18] and photonic sintering.^[17]

Recently, microwave flash sintering was investigated as a fast alternative technique to sinter nanoparticle features. In general, it is believed that the interaction between microwave radiation and conductive materials is based on Maxwell-Wagner polarization, which results from the accumulation of charge at the materials interface, eddy currents and electric conduction. On the other hand, the absorption of microwave radiation of thermoplastic polymers is insignificant due to limited polarization of dipoles below their glass transition temperature. As a consequence, conductive particles can be sintered selectively whilst the substrate remains unaffected. For sufficient sintering by microwave irradiation, a low initial conductivity is required, which was obtained *via* a mild thermal treatment^[18] (Fig 1a). Since the thermal pre-treatment times are not compatible with R2R production speeds, the pre-sintering was performed via a photonic flash sintering method (Fig 1b).^[7]

Photonic sintering uses pulses of intense light that have a broad spectrum in the visible range. The mechanism of photonic sintering is based on a thermal conversion of the metal precursor into its conductive counterparts, caused by the high intensity of the flash lamp.^[19] Photonic sintering irradiates the entire sample with multiple short flashes, which is in contrast to conventional thermal sintering, where the sample is exposed continuously to a high temperature.

Only the dark-colored as-printed ink absorbs the radiant energy of the lamp, while the absorption of radiation by the underlying polymer foil is negligible. Since the polymer substrate is a poor heat conductor, the hot silver film will heat the substrate only at the interface region. The absorbed energy raises the temperature in the ink in a very short time and causes a rapid sintering of the metal precursor. By delivering a sufficient amount of energy to the system, hence by carefully controlling the intensity of the lamp, the pulse length, as well the number of flashes, the temperature inside the as-printed ink can be maintained at a constant value, without causing damage to the underlying substrate.^[17] Photonic sintering of the as-printed lines revealed conductivity values up to 28% of bulk silver within 10 seconds. Longer sintering times did not improve the conductivity, but rather resulted in damaging the substrate since

too much energy was absorbed by the samples, which was dissipated into the substrate and, as a consequence, heated it above its glass transition temperature. At this point, the absorption of visible light is limited due to the reflective appearance of the sintered features. However, the absorption of microwaves is enhanced due to the conductance of the particles. Therefore, microwave flash sintering was used to further sinter the photonic pre-sintered features.

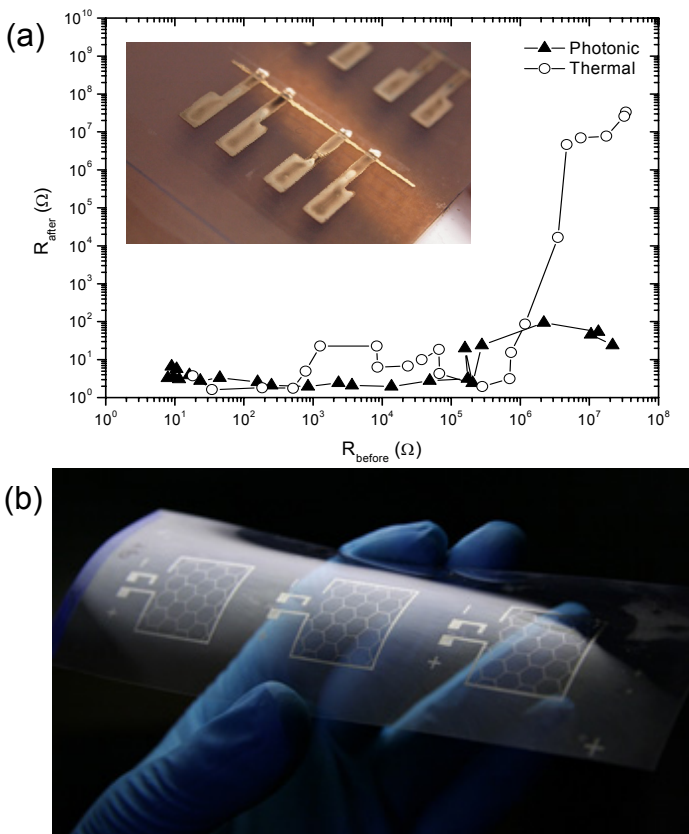


Figure 2. Effect of the initial line resistance (R_{before}) on the resistance obtained after microwave flash exposure (R_{after}) of one second for either a thermal or a photonic pre-treatment. The inset shows a macro-photograph of a typical sample with four inkjet printed antennae and a single line of 7 mm length and 500 μm width printed on top (a); Inkjet printed template sintered using R2R photonic sintering followed by microwave flash sintering. Reprinted from reference 7.

By using visible light photonic pre-sintering, followed by an one second microwave flash exposure, the features revealed final conductivities of up to 40% of bulk silver.^[7] The combination of two flash sintering techniques enabled the as-printed wet features to be sintered within 15 seconds. The obtained conductive features can be used for OLED (Fig 2b) and OPV applications.

Inkjet printing of light emitting polymers

Besides the creation of electrically conductive features, also the deposition of active layers, such as light emitting polymers for OLED applications is of great importance for the manufacturing process of organic electronic devices. Typically, such materials are not compatible with state of the art vapor deposition methods that

are used for the application of inorganic materials or small organic molecules. In contrast to these methods, solution deposition techniques represent a cost-effective alternative due to their potential applicability to R2R production processes using flexible substrates.^[20] Deposition techniques from solution are enabled by the attachment of side chains to the backbone of π -conjugated polymers, which provides the required solubility in organic solvents.

One of the most promising solution deposition techniques to process, for instance light emitting polymers like poly(phenylene-ethynylene)-poly(phenylene-vinylene) (PPE-PPV) copolymers, is inkjet printing.^[21] In order to produce homogeneous films many parameters that affect the final layer quality require an optimization. The control over film formation can be achieved by the variation of ink concentration, solvent system, substrate temperature as well as drop-to-drop distance (dot spacing). Inkjet printing enables a combinatorial screening of thin-film properties of polymer layers that strongly depend on the ink and the processing parameters.^[22] Inkjet printing is, therefore, a suitable technique for the evaluation of synergies between ink and film properties. Characterized by an efficient materials handling, both time and energy can be saved using inkjet printing as a deposition technique.

Although inkjet printing offers several advantages compared to other techniques, including a high material-efficiency, a low waste production and a mask-less, digital processing,^[22] it is not an established technique for the deposition of polymer materials, yet.^[4, 23] Reasons can be found in the challenges that arise while using inkjet printing, such as the limitation to printable solvents and the control over the drying processes as well as the limitation of the printing speed. The coffee-drop-effect^[24] and the Marangoni flow^[25] are often causing an uneven evaporation of the wet feature, resulting in non-homogeneous final structures. An optimization of the ink as well as the processing parameters is required for each polymer class in order to identify optimal printing parameters for a specific application. Furthermore, not only the film formation properties, but also the optical characteristics of the layers are of importance when applying different processing parameters. In addition, it was found that the emission color of inkjet printed films is significantly influenced by the layer thickness.^[26] In order to tune the optical properties of printed films, the chemistry of the used polymers can be tailored by the introduction of donor-acceptor dyes or by altering the length of the polymer chain. In general, the tunable band gap allows the synthesis of π -conjugated polymers with tailored optical and mechanical properties.^[27]

By chemical tailoring of the polymers it is possible to adjust the emission spectra in order to obtain red, green and blue (RGB) color. For this purpose, different polymers including a poly(fluorene-phenylene), a poly(phenylene-vinylene) (PPV) and a poly(phenylene-ethynylene)-poly(phenylene-vinylene) (PPE-PPV) copolymer were synthesized (Fig. 3), which were investigated for their solution properties, inkjet printability and film formation characteristics.^[28] All investigated polymers are soluble in a solvent system of toluene/*ortho*-dichlorobenzene (*o*-DCB) in different concentrations. The solvents were used in a ratio of toluene/*o*-DCB 90/10, which is known for printing of polymers for solar cell applications.^[21]

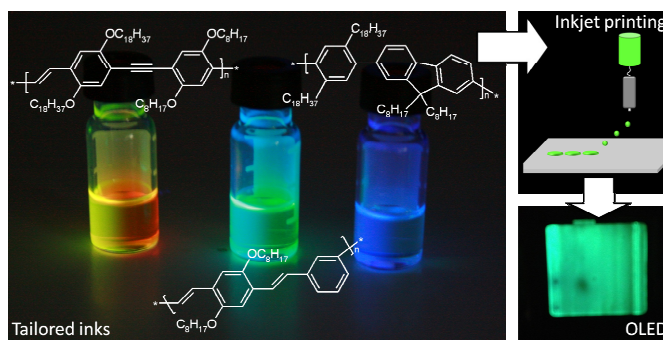


Figure 3. Conjugated polymers with tailored emission spectra, matching orange-red, green and blue (RGB) emission, were synthesized and their film formation properties were optimized via a combinatorial screening workflow using inkjet printing. The optimized inkjet printed polymer layers were used as active layers for OLED devices. Reprinted from reference 28.

For the fabrication of the emissive layer of an OLED a film thickness of approximately 80 nm is required to achieve good light emitting efficiencies. For the investigation of film formation, film thickness as well as film roughness, the solution of the red-emitting polymer was optimized in terms of polymer concentration and dot spacing. It was found that a concentration of 4 mg/mL and a dot spacing of 140 μm resulted in homogeneous films with the required thickness of 80 nm. Due to similar ink properties of all investigated polymers, e.g. density, surface tension and viscosity, the optimized printing conditions found for the red-emitting polymer were also applied to the green as well as the blue emitting polymer in order to deposit uniform films with defined thicknesses. From these polymers, OLEDs with a size of 1 \times 1 mm² and 3 \times 3 mm² were prepared by using the optimized printing conditions found for each polymer. When printing larger OLEDs with a size of 20 \times 30 mm² a limitation of inkjet printing could be observed when using a single nozzle print head. As the films are prepared by a line-by-line deposition, the size of an inkjet printed film is crucial for the drying process, since the lines start to dry before printing of the entire film is completed, resulting in a large surface roughness and inhomogeneity.

The results obtained here represent a significant step towards a controlled and predictable film formation by means of inkjet printing for OLED applications. In the near future, a parallel printing of the three different inks may be possible using a multi-nozzle system, which will allow a speed-up and scale-up of processing the active layers for OLEDs.

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