Towards High speed Inkjet Printed Electronics – Technology Transfer from S2S to R2R Production

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Abstract

An economically successful implementation of printed electronics technologies in industrial production processes requires high throughput and large scale compatible manufacturing techniques. Roll-to-roll inkjet printing and photonic sintering of metal-based conductive inks on flexible plastic substrates is a promising approach in this respect. It is, however, currently mainly applied on a small scale sheet-to-sheet basis, and technology transfer towards roll-to-roll production has proven to be challenging. Presented here is a stepwise strategy, starting with rather basic, laboratory scale equipment and using small amounts of materials. Based on the outcome of these tests, the experimental scale is successively enlarged and the process conditions continuously optimised, until finally industrial applicability is convincingly demonstrated on a pre-pilot roll-to-roll production line with manufacturing rates of up to 20 m/min. Following this stepwise approach, we were able to scale up the production speed by several orders of magnitude in a purposeful and thus cost and labour efficient way.

Introduction

Inkjet printing is a popular deposition technology due to its flexibility, non-contact approach and economic use of (potentially expensive) ink materials in drop-on-demand systems [1,2]. For many years, it has been a widely used fabrication technique in the graphics industry for decorative purposes. More recently, its potential for technically more demanding applications like the production of functional electronic devices, has been demonstrated in a variety of academic and industrial research laboratories [3,4]. These examples are, however, mainly restricted to small numbers of functional devices produced on a sheet-to-sheet (S2S) basis. In order to be applicable on industrial production scales, faster, cheaper and preferably continuous technologies need to be developed, as they are already standard in the graphics inkjet industry. In other words, the step from S2S towards roll-to-roll (R2R) manufacturing needs to be done in order to achieve economically viable high-volume production processes [5]. The high functional demands of printed electronic devices, however, have until now posed serious restrictions on the successful implementation of R2R fabrication on a large scale and in a commercially profitable manner, although some promising results in this direction have recently been reported [6,7]. The research presented here aims at building up experience and knowledge on a small scale S2S basis and transfer it via large scale S2S equipment finally to a R2R pilot production line. At every step, the next higher one can be mimicked in order to carry out the necessary optimisations without actually working already on such large scale and potentially wasting large amounts of materials.

The process we have chosen to study is the production of metallic patterns with high electrical conductivities on low cost polymeric foils such as polyesters. These form a core ingredient of many large-area printed electronic devices, such as organic light emitting diodes (OLEDs) and organic photovoltaic cells (OPVs). Their typical purpose is to serve as shunting lines and current collecting grids, reducing the sheet resistance of transparent electrodes made from conductive oxides or polymers [6-8]. Furthermore, similar metal structures are also required in thin film transistors (TFTs), RFID tags, smart packaging, and a number of other printed electronics applications [9,10]. Inkjet printing and sintering of metal-containing inks (based on nanoparticles or metal-organic decomposition complexes) is one possible solution [11].

Experimental Part

Materials

All experiments described here were carried out using a commercially available conductive inkjet formulation provided by Sun Chemical, United Kingdom (Suntronic U5603). It is a dispersion of silver nanoparticles (silver content 20 wt%, average particle size 30 – 50 nm) in a mixture of polar solvents (mainly ethanol, ethylene glycol and glycerol). The particles are stabilised by a polymeric shell which suppresses aggregation. The viscosity is specified to 10 – 13 mPas, and the surface tension to 27 – 31 mN/m, which are both in the typical range for jettable fluids [12]. Prior to use, the ink was sonicated and filtered through 0.45 micron Teflon syringe filters. For printing experiments on the LP50 setup (vide infra), 10 vol% of ethylene glycol (extra pure, Sigma-Aldrich, The Netherlands) needed to be added to the ink.

The substrates used were commercially available poly(ethylene naphthalate) (PEN) foil (Teonex Q65FA, DuPont Teijin Films, The Netherlands) and a semi-finished poly(ethylene terephthalate) (PET) product (PET with V109 coating, Agfa-Gevaert, Belgium). For the experiments, the side without the V109 coating was used. Film thickness is 125 microns in both cases.

Equipment

Printing process optimisation was done successively on a small-scale S2S materials inkjet printer (DMP-2831 from Fujifilm Dimatix, United States), a large-scale S2S research inkjet printer (PiXDRO LP50 from OTB Solar – Roth & Rau, The Netherlands), and a customised industrial R2R inkjet print module (from Stork Prints B. V., The Netherlands). The DMP printer uses nonrefillable cartridges (DMC-11610 from Dimatix, United States). The print head contains 16 parallel squared nozzles with a diameter of 30 micron, resulting in a droplet volume of 10 pl. The LP50 printer is equipped with a KM512S printhead (Konika Minolta, Japan) with 512 nozzles and produces droplets with a size of 6 pl. In the R2R print module from Stork Prints B. V., a 1001 GS6 printhead from Xaar, Sweden, is built in, which has 1001 nozzles and can produce seven droplet sizes ranging from 6 to 42 pl.

For sintering process optimisation, three self-constructed photonic flash sintering units of increasing size and complexity were employed. The construction principles are revealed in [13]. The smallest one was a so-called stand-alone tool consisting of a single tubular Xenon flash lamp (XOP-15 from Philips, The Netherlands) placed in the focus line of a reflector tube with elliptical cross section. It allows real time monitoring of the resistance and temperature of a single printed test line during exposure to highly focussed flash light with up to 1000 measurement points per second [14]. The lamp is steered by a specifically designed software based on Labview. It emits radiation ranging from 400 to 800 nm. Light intensity and flashing frequency can be varied independently, whereas the pulse duration has been shown to be a function of the used intensity. More complex patterns than single flashes with a fixed frequency are also possible, e. g. bursts of several high-frequency pulses followed by longer cool-down periods. Finally, the flashing conditions can be programmed in such a way that they change during the process.

The next more complex tool is a S2S sintering unit comprising a sequence of two elliptic reflectors with one XOP-15 lamp each, and a Sinteron 2000 lamp from Xenon Corp., United States. The latter lamp was used at a fixed frequency of 1.8 Hz and a pulse length of 2 ms, the intensity being varied. Its emission spectrum ranges from 240 to 1000 nm. All three lamps can be controlled and steered individually. A substrate holder can move through the plane of their common focus lines at a predefined speed between 0 and 20 m/min. This apparatus can handle complex patterns printed on substrates of up to 30 x 30 cm size. For single lines, also real-time in-line resistance and temperature measurements are possible.

The R2R flash sintering setup is constructed according to very much the same principle, except that it is mounted on a R2R line, which allows the continuous processing of flexible substrates of up to 30 cm width at speeds up to 20 m/min. It is equipped with a near-infrared drying unit (NIR 120-M3) from Adphos, Germany, a set of up to four XOP-15 lamps (arranged opposite to each other to enable illumination from the top and bottom) and one Sinteron 500 lamp from Xenon Corp. United States. This lamp was used at a fixed frequency of 1.8 Hz and a pulse length of 0.5 ms, the intensity being varied. Its emission spectrum ranges from 240 to 1000 nm. All six energy sources can be individually controlled.

For pre-drying samples and for reference reasons, thermal treatment was also carried out, using hot air oven (FD53) from Binder, Germany.

Results and Discussion

General strategy

As mentioned in the introduction, optimising printing and sintering conditions of conductive inks to meet the stringent quality requirements of large scale printed electronics applications is a complex task. As a consequence of its frequently high time consumption and materials usage, it can be very costly, e. g. given the fact that most conductive inks are based on silver and therefore rather expensive. A structured and efficient experimental strategy towards scaling up the production under optimised processing conditions is therefore highly desirable.

In this contribution, we present a stepwise approach, during which the applied conditions and the used setup successively resemble more closely those of an industrial R2R production line. Starting with a rather broad range of fast and small-scale printing and sintering tests, an overview can be obtained about promising materials and processing conditions. In a following step, these initial results can be used as starting point for a next optimisation round on larger scale, already more closely mimicking the final R2R processes. Finally, the entire process is fine-tuned on a R2R pilot production line, to achieve insight into the process under conditions which resemble the industrial high throughput production environment as closely as possible and therefore legitimate the substantial investment in terms of time and materials they require.

Ink selection

As a first step, a number of different commercially available conductive inks were benchmarked on small scale on the Dimatix printer according to a standardised testing procedure. Key performance parameters that were checked included ink shelf lifetime, jetting reliability and stability (minimised nozzle failure and satellite formation for a selection of different jetting waveforms), the interactions with the inks with a number of relevant substrates (wetting and spreading behaviour, adhesion), speed of thermal drying and sintering and the final properties of the printed structures (line morphology and roughness, electrical conductivity). Non-technical selection criteria included reliable availability also of larger quantities and materials cost. From this testing procedure, the Suntronic U5603 formulation emerged as the product showing the most promising overall performance, and was therefore chosen for all further optimisation and scale-up experiments.

Optimisation of the processing conditions

The printing performance of the chosen Suntronic U5603 ink was then fine-tuned on small scale using the DMP printer by systematic optimisation of the waveform to achieve the most stable jetting behaviour. Furthermore, the drop spacing and number of printed layers can be varied to optimise the line morphology. Using these optimised deposition conditions, well-defined lines with widths down to 70 microns could be produced on PEN. After thermal sintering for 15 minutes at 130 ^{o}C, line heights of ca. 250 nm and conductivities of $4.4 \cdot 10^6$ S/m (corresponding to 7 % of the bulk silver value) were obtained. Increasing the temperature to 150 ^{o}C gave an improvement to 10 % bulk silver conductivity. Broader structures (200 or 500 microns) usually resulted in increased line heights (up to 500 nm) due to relatively less spreading, and higher conductivities (up to 15 % bulk Ag), but at the same time significant foil deformation was observed.

Sample lines were subsequently printed on PEN substrates and their photonic sintering behaviour tested in a stand-alone unit [14]. It consists of a single tubular Xenon flash lamp placed in the focus line of a reflector tube with an elliptical cross section (Fig. 1). As the ink test line is exactly placed into the second focus line of the reflector, high energy densities are possible without the need for extremely powerful lamps. The differences in absorption spectra between ink and substrate ensure selective heating of the ink, and excessive indirect heating of the foil is prevented by applying the photonic energy in very short pulses. By systematically varying flashing parameters like pulse intensity, frequency, and flash patterns, and by monitoring the electrical resistance and temperature in the test lines, optimised sintering conditions can be determined which combine fast sintering with acceptably low foil deformation (Fig. 2).

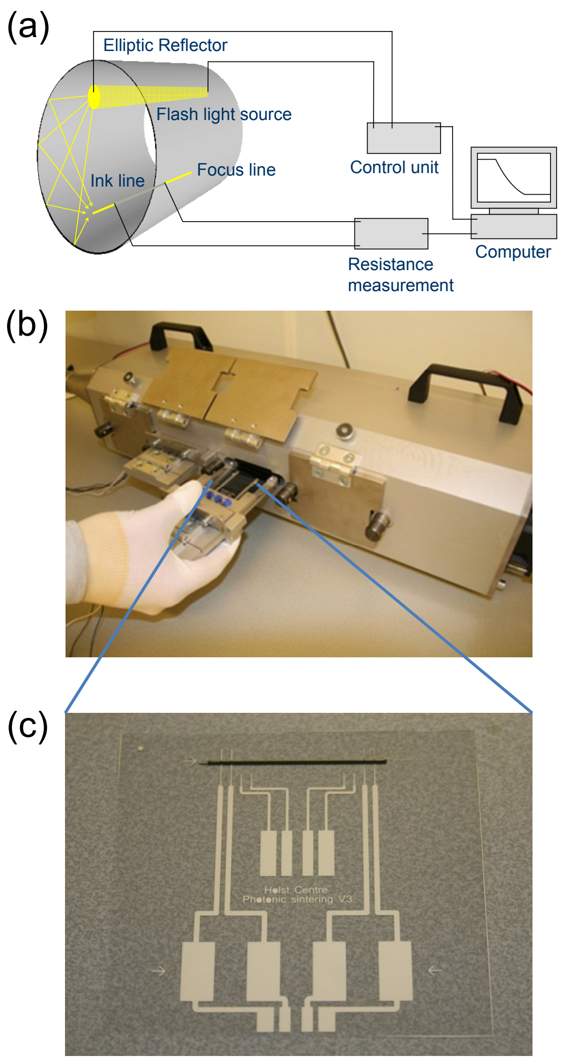

Figure 1. *Construction principle (a) and photograph (b) of the stand-alone photonic sintering unit. (c) Four point probe for resistance and temperature measurements, with a wet (black) test ink line.*

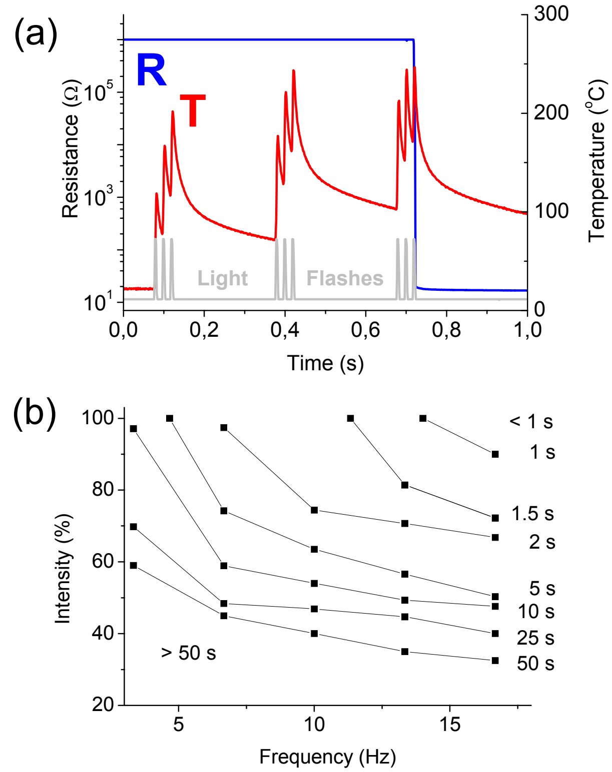

Figure 2. *Resistance and temperature measurement during photonic flash sintering (a). Sintering time as a function of flashing intensity and frequency (b).*

Using identical printing conditions as mentioned above for the thermally sintered reference samples, photonic sintering resulted in even smaller line widths of down to 60 microns and the same conductivity (7 % of the bulk silver value) as after 15 minutes at 130 ^{o}C. Photonic sintering, however, accelerated the entire process by two orders of magnitude, and in neither case signs of foil deformation were observed.

Both the optimised printing and sintering parameters from these small-scale experiments served as input for the next step, which was the extension from single lines to complex and potentially functional two dimensional patterns of up to 30 by 30 cm large substrates. The LP50 printer used for this needs considerably larger quantities of ink than the DMP (about a factor ten more), and by choosing a well-considered starting point, time and materials savings can be significant. Finally, it turned out that for an optimal printing performance, the ink formulation needed to be adjusted by addition of 10 vol% ethylene glycol.

Photonic sintering under R2R conditions can be mimicked by the S2S sintering unit, since the substrate with the ink on it can be moved through the common focus lines of an array of flash lamps at a predefined speed. The flashing parameters of each lamp can be individually controlled, in order to achieve the most efficient incoupling of energy into the printed structures. In addition, a number of different lamp types can be used, to account for differences in the absorption spectra of various inks and foils.

After process parameter optimisation, a two-dimensional test pattern was printed, testing different line widths and orientations with respect to the printing direction, as well as some functional structures (Fig. 3). Minimum line widths of 75 microns and line heights of ca. 350 nm height were obtained with conductivities of about 11 % bulk silver at a substrate speed of 30 cm/min. For industrial R2R applications, this speed is still very slow, which is due to the limited number of lamps present in the S2S unit.

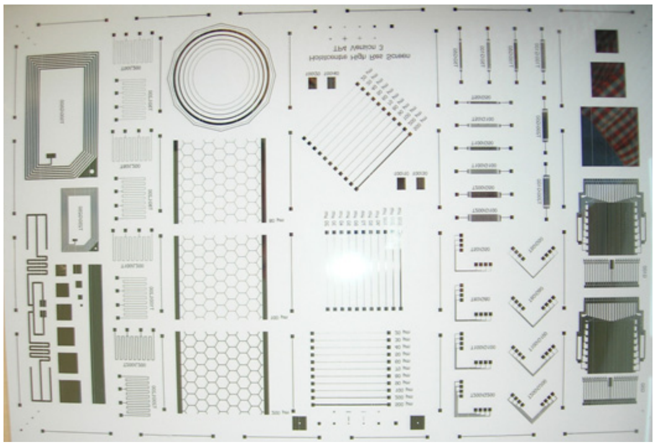

***Figure 3**. Test pattern used for process optimisation on the LP50 and the S2S photonic sinter tool.*

The final step towards industrial processing conditions was set by transferring the results achieved by the S2S experiments to a pre-pilot R2R line, equipped with an industrial inkjet module and a photonic sintering unit similar to the one used in the S2S setup (Fig. 4). It is, however, equipped with a larger set of lamps, enabling higher processing speeds. Again, the optimised S2S conditions served as starting point for further process optimisation, and as in the case of the earlier example, this approach proved highly efficient. At a substrate speed of 4 m/min, the ink could be printed and sintered to achieve conductivities of 15 % of the bulk silver value. Printing and drying was demonstrated up to 20 m/min, but in this case, more process optimisation is necessary for satisfying conductivities.

Conclusions

R2R inkjet printing in combination with photonic sintering has a promising potential to be applied for the production of printed electronic devices on an industrial scale. In order to achieve a reliable, stable and fast manufacturing process, which is an indispensable prerequisite for successful commercial application, intense process optimisation has to be carried out. A stepwise approach has been demonstrated to be highly efficient in order to reach this goal. We start testing on small scale a broad value range of the parameters under investigation, and consecutively the studied range is narrowed down, while at the same time enlarging the scale of the experiments to more closely resemble to final industrial process conditions. This strategy is highly efficient in terms of time and materials consumption and has enabled us to develop a pre-pilot production process that can serve as a starting point for the implementation of this technology in an industrial production environment.

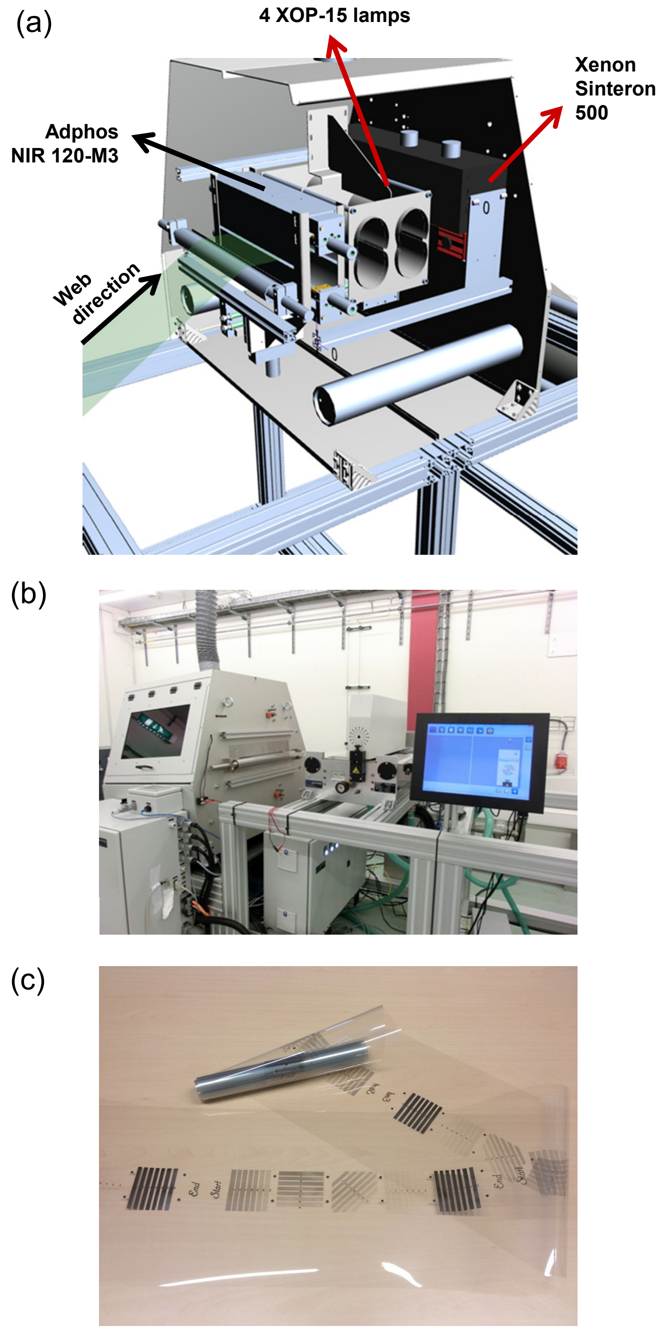

***Figure 4**. Construction principle (a) and photograph (b) of the R2R compatible photonic sintering unit. The latter picture also shows the industrial inkjet printing unit.(c) Sample of PET foil with inkjet printed and photonically sintered test pattern of silver ink produced on the R2R setup.*

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Author Biography

Pit Teunissen finished his B.Sc. in 1999 and subsequently joined the group of Prof. D. J. Broer at Eindhoven University of Technology where he participated in various research projects on functional polymers. In 2006 he started a position at the Polymer Technology Group B.V. as a research fellow, working on inkjet-printing of liquid crystals for security and sensor applications. Since 2011, he is a process engineer at Holst Centre for inkjet-printing of conductive structures for OLED, OPV, RFID and smart label applications.