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PROJECT FINAL REPORT

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Project acronym: LOTUS

Project title: Low-cost highly conductive high resolution structures for flexible large area electronics by high throughput low temperature processing

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Final publishable summary report

The final publishable summary report consists of four sections:

- Executive summary
- Project context and objectives
- Address of project public website and contact details
- Main S&T results

Executive summary

The LOTUS proposal addressed the urgent need for a technology to produce the highly conductive patterns required for high throughput, large volume manufacturing of flexible large area electronics. While all printed electronics need “electric wiring”, LOTUS specifically targeted the applications which have advanced the most towards commercialization: flexible thin-film photovoltaics (PVs), Radio Frequency Identification (RFIDs), and Organic Light Emitting Diode (OLEDs) for lighting.

The general objective was to provide a simple, low cost, energy-efficient, environmentally friendly and roll-to-roll (R2R) compatible platform to produce highly conductive structures with high resolution. The interplay between materials researchers, technology developers and end-users allowed to generate solutions quickly and effectively with minimum investment and time and to achieve maximum output with minimum risk. This will also accelerate the transfer to mass production. The strategy was based on an integrated approach to address both the common needs and the specific requirements of the most representative applications.

Highlights of the project were the development of Ag-, Cu- and Al-based inks. The Ag-based inks can be produced at a price of approximately EUR 1,000.- whereas commercially available Ag-based inks are much more expensive, the price being about EUR 6,000.- Cu-based inks were developed at lab scale whereas Al-based inks are so reactive with oxygen and water that they can only be used under a protective atmosphere thereby making it very hard to print on a R2R line. Furthermore, it proved to be difficult to perform the printing and sintering on flexible substrates for the PV and OLED demonstrators, but all three demonstrators were finished and fully functional. Another highlight was the development of a R2R integration of inkjet printing and sintering which will be commercialized in the near future. With this R2R line already RFID antennas were printed which have the same performance at less than 50% of the usual materials usage. A working model was developed for drying, sintering and resistivity prediction. Finally, a first completely backend contacted CIGS module was manufactured using the technologies and facilities developed in this LOTUS project.

The platform developed will reinforce the leading position of the European Industry in flexible OLEDs, PVs, and RFIDs. Moreover, it will be beneficial to any flexible electronics including thin-film transistors, power converters, flexible batteries, printed sensors for biomedical use (point-of-care) and food protection/freshness applications. These devices presently at various stages of development also need an “electric wiring”. Thus the LOTUS project results will contribute to wealth creation and making new technology available to address societal needs. The technologies and materials generated will enable the European Community to be competitive with Asian and North American products (there are presently no conductive inks and sintering tools manufacturers in Europe). The LOTUS project created synergies and cooperation between research groups, equipment manufacturers and end-users bringing them to the position of global frontrunners in their respective technology areas. As a result of this, a new EU project is being discussed with several of the partners. In addition, bilateral projects between partners are under discussion, in which results of this LOTUS project will be applied.

Summary description of project context and objectives

IDTechEx estimates[2] that the market for printed and potentially printed electronics, including organics, inorganics and composites, will reach $57.16 billion in 2019 with 76% printed and 73% on flexible substrates. Indeed the progress recorded so far in development of flexible electronics opens the way towards mass production and implementation in the daily life. However, the transition from small scale demonstrators to large area prototypes and up-scaling to large volume manufacturing reveals new unforeseen challenges from technical as well as economic standpoints. A very important element of all electronic devices is the conductive structure that connects different components, the "electric wiring". While all the electronic devices need such "electric wiring", the requirements may vary according to their specific function and application. Flexible OLEDs, photovoltaics and RFIDs appear to be the applications the most advanced towards commercialization though more effort is clearly needed to develop adequate manufacturing processes. Although, they serve different purposes and have different working principles the three applications have common needs when it comes to the "electric wiring".
The major common requirement is a **reliable cost-effective technology able to produce highly conductive tracks with high resolution features.**
The existing technologies have been stretched to their limits but none proved able to provide the needed solution. Some as photolithography or laser ablation transfer fulfil the technical requirements (conductivity, feature size) but are complex cost-prohibitive and environmentally unfriendly. Others are more affordable and less polluting but do not meet yet the technical requirements (screen printed silver-flakes inks). The latest developments indicate that the conductive inks may offer the solution looked for, but more and immediate effort is needed to bring the technology to the required level of performance. On the other hand the three applications have also **specific needs** as the common "electric wiring" may be called upon to play more than just a simple "connector" role. Moreover, the conductive structures are integrated in multiple layer devices and the overall performance and functioning of the device depends on the compatibility at interfacial level.

LOTUS project aims at providing the materials and the technology needed to produce the "electric wiring" in the flexible large area electronics by addressing in an integrated approach both the common needs and the specific requirements of the most representative applications.

The requirements and needs of the selected applications in the present European and global context are summarized below.

OLEDs for lighting – context and requirements

As the traditional light bulbs are being gradually phased out (in EU by 2012) there is a worldwide need for alternative low-cost lighting devices. The success registered over the past few years indicates that OLEDs are the ideal candidate for the future lighting. Research towards R2R fabrication of large area lighting devices emphasizes the need for a highly conductive grid (so-called "shunting lines") as a key component in order to ensure a homogeneous distribution of the current within the device and prevent the voltage drops that lead to fading light intensity along the anode plane (Figure 1). Secondly, in the OLED lighting devices the current needs to "enter" the lighting area. For this a highly conductive high current density circuit is needed around the lighting device. Also known as the "bus bar system", it is in most of the cases located outside the working area of the lighting device and connected with the conductive grid located inside. The challenge is to produce (ideally via printing) both the shunt lines and the bus bars in one step to lower the manufacturing costs and avoid potential barrier issues. With a bus bar system that combine high conductivity and small features the "wasted" area would be minimized. In addition the conductive grid is sandwiched between an organic and inorganic layer which might results in unpredicted and undesirable chemical compatibilities, shortcuts, etc. that need to be addressed. The switch from rigid to flexible substrates devices is accompanied by additional requirements in terms of flexibility and bendability. Use of flexible low-cost substrates bring to the fore additional challenges as it is limited to processing at low temperatures (<150ºC).

[2] http://www.idtechex.com/research/reports/printed_organic_and_flexible_electronics_forecasts_players_and_opportunities_2009_2029_000219.asp

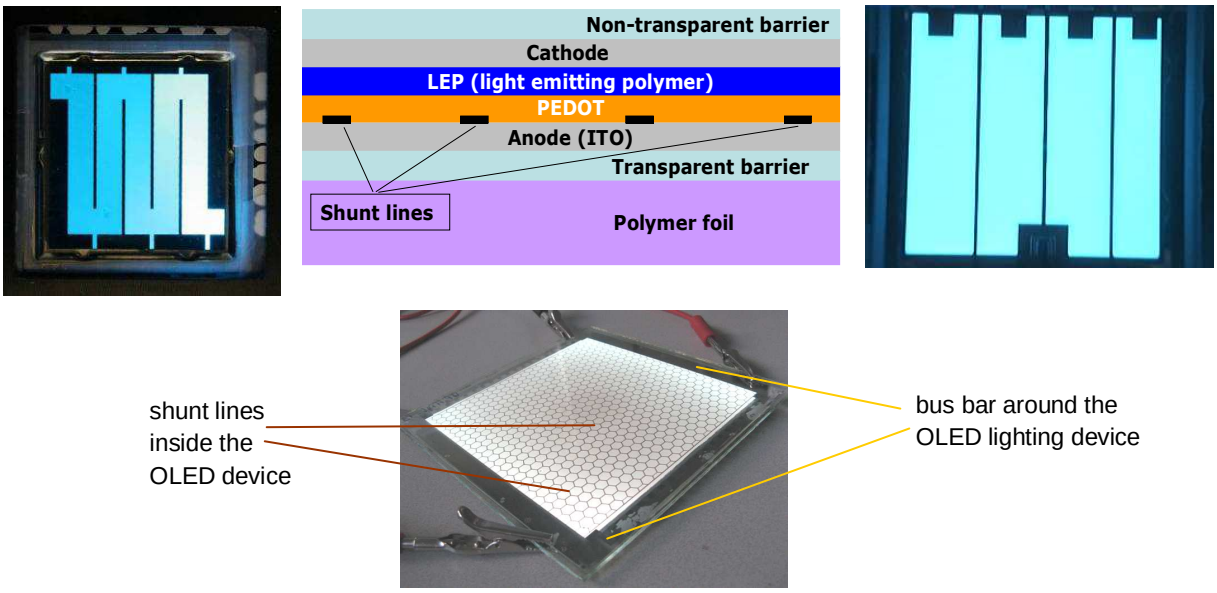

Figure 1: Upper left - OLED without shunt lines, middle - multilayer structure of OLED devices, right - OLED with shunt lines; lower middle - shunt lines (inside) and bus bar (outside) the OLED device

Flexible thin-film photovoltaic (PV) - context and requirements

In the effort to reach the 2020 target of the European Union to generate 20% of the electricity by renewable energy sources, photovoltaic will play a crucial role. The PV market has seen a rapid expansion in recent years with annual growth rates exceeding 50%. Also in the current financial crisis, the renewable energy sector is identified as one of the key future growth markets. Thin-film technologies have the potential to significantly reduce production cost and finally achieve the so called 'grid parity', when electricity generated by PV will be competitive to consumer electricity prices. Similarly to OLED-based lighting devices, the "electric wiring" in the photovoltaic cells plays a double role. First, a fine highly conductive grid (similar to Figure 1) is needed to improve the collection of the photon generated charges by the TCO (transparent conductive organic) layer. The requirements for the conductive grid in thin-film PV are quite similar to the ones above-mentioned for the OLED-based lighting devices. Unlike the OLED-based lighting devices in the PV cells, high currents are generated and the conductive grid has to fulfil this additional demand and limit or suppress the ohmic resistance losses within the cell. Second, several sub-devices need to be connected in series in order to increase the voltage of the large-area devices (Figure 2). While for glass based thin-film PV, monolithic series interconnection processes are readily available, these concepts cannot directly be transferred to foil based PV modules. A unique requirement for the current collection and monolithic series interconnection on flexible substrates is a printed metallization, for which the present solutions – which in most cases are not even accessible on the market as they are proprietary developments of individual PV producing companies (many of them located in US) - lack behind the requirements for performance, cost and compatibility with high-throughput manufacturing.

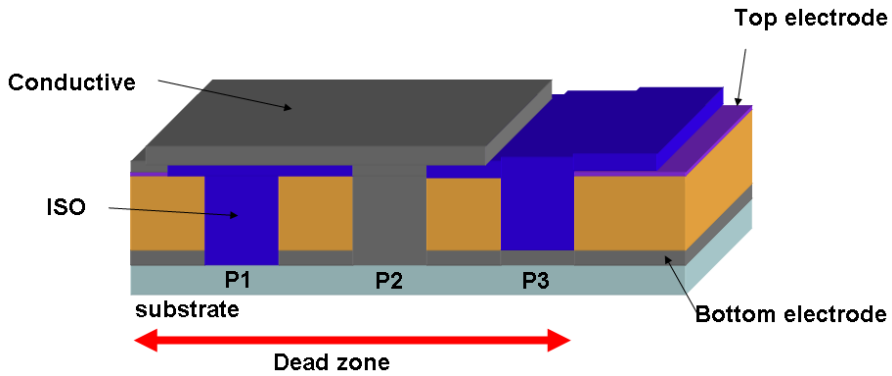

Figure 2: Interconnects of the flexible thin-film PV modules

The main challenges for both, organic and inorganic flexible thin-film PV are to print the current collecting and interconnecting metallization in a continuous large-area and high throughput R2R process on temperature sensitive substrates and/or active materials while aiming at the highest possible conductivity. Like OLEDs PV cells are multi-layered devices whose overall performance might be affected by incompatibilities between the conductive structures and the materials in the adjacent layers. As the materials and interfaces in the PV devices in the PV devices are different from the one used in OLEDs both applications have to be investigated as the requirements for the chemical compatibility might differ.

RFIDs (Radio Frequency Identification) – context and requirements

A smart and simple system, RFID has great potential to radically change more than just a routine in our daily lives. The technology has been available for more than fifty years but it has only been recently that the ability to manufacture the RFID devices has fallen to the point where they can be used as a "throwaway" inventory or control device. While the potential payoffs of implementing RFID-based tracking systems are enormous so are the challenges involved in those implementations. Europe and USA are the big players in the RFID market and for both one of the major challenges in the widespread use of RFID for retail solutions is cost. Tremendous effort is put into developing an all-printed RFID device as a pathway toward the realization of ultralow-cost RFIDs because the antenna can be printed and attached to the chip in a single continuous printing step. This would provide value-added RFID technology at a minimum cost by producing components in line with traditional package printing.

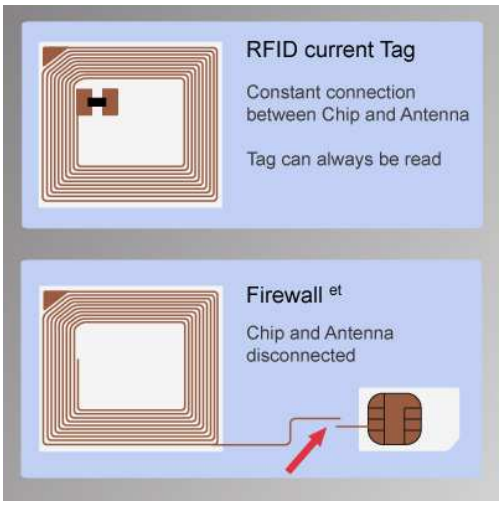

Figure 3: Various RFID tag layouts

However, for such a process to be successful low-resistance printed conductors are crucial as they have to provide enough conductivity to enable the chip to receive power from the reader and send back a signal. The read distance of RFID tags decreases with less conductive antenna traces. The main RFID applications are based on two frequency bands HF communication band at 13.56 MHz and UHF in the range of 868 MHz to 950 MHz and for both highly conductive antenna tracks are required. Significant conductivity gains, tailored surfaces and process flexibility will enable manufacturers to take advantage of thinner films and achieve longer read distances at improved cost. Conductive inks are cost-effective for RFIDs in two ways. The material cost of inks can be much lower than that of traditional stamped or etched metal antennas, even when silver-based inks are considered. Stamping and etching processes are considered subtractive, because they discard unused metal. Since high-speed printing processes are both fast and additive, applying a conductive ink antenna or circuit can be significantly less expensive and faster than the alternatives. Though, these advantages are presently mitigated by the low conductivity achievable with the post-deposition (thermal sintering) treatment available.

Scientific and technological objectives

The goals of the LOTUS project have been set up in such a way as to meet both common and specific needs of the targeted applications: OLEDs for lighting, flexible thin-film photovoltaic and RFIDs.
The general objective of the LOTUS project is to establish a cost-effective energy efficient high throughput platform to generate highly conductive structures for flexible large area electronic devices with the following minimum specifications:

- resistivity: $\leq$ 2-3 bulk silver
- line width: $\leq$ 50 µm
- deposition and processing rate: $\geq$ 20 m/min
- processing temperature: <150ºC

- web width: 30 cm
- bendability: bending radius 20 mm

The main goal is to form highly conductive patterns via a tandem process consisting of a deposition technique that allows patterning of very fine and well defined (high resolution) structures and a post deposition treatment fully compatible with R2R manufacturing. Both materials and processes involved will be tailored for use on low-cost traditional substrates (plastic, paper) and/or sensitive active materials (organic/inorganic) in the final device.
In order to reach the final target several objectives have to be attained:

1. **INKS:** metal precursors (nano-sized particles and organic complexes) able to readily form highly conductive (≤ 3x bulk metal) patterns have to be synthesized and formulated into highly performing inkjet inks
   Transfer to mass production: evaluate and assess the industrial aspects related to the transfer of the conductive inks and metal precursors from lab scale to mass production

2. **PROCESSING:**
   Patterning / Inkjet printing: the process has to be developed to combine the speed and flexibility of printing with the precision of standard lithographic methods:
   < 50 µm at linear speed ≥ 20 m/min
   Sintering techniques: have to be brought to adequate level of performance to obtain high conductivity (≤ 3x resistivity of bulk metal) in ~2-3 sec at linear speeds of ≥ 20m/min without damaging the temperature sensitive substrates or other active materials in the final device.

   The above tandem patterning **inkjet printing - sintering** platform has to be transferred to R2R pre-pilot and its reliability assessed.

3. **PREDICTIVE THEORETICAL MODELS:** have to be developed to gain a better understanding of the sintering process and its mechanism and help optimization of the process and the materials (metal precursors and inks)

4. **SPECIFIC ISSUES related to INTEGRATION** of the materials and processes developed in the final devices have to be evaluated to ensure a high level of performance of the multilayer devices

5. **DEMONSTRATORS:** will be produced as a proof of the capabilities and the performance of the materials and processes developed

6. The **ECONOMIC** and **ENVIRONMENTAL GOAL** of the LOTUS project is to establish a cost-effective energy efficient and environmentally friendly technology

By achieving the above mentioned scientific and technological objectives LOTUS will reach its general objective

low-cost high throughput (R2R) platforms and processes) to produce highly conductive structures with high resolution “electric wiring” for large area flexible electronics

Address of project public website and contact details

http://www.lotus-fp7.eu

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Main S&T results

Main objectives of WP1

- Explore synthetic routes and establish preparation procedures for the metal precursors.
- Develop metal precursors and formulate them into inkjet printable inks with potential to generate highly conductive patterns under mild conditions compatible with temperature-sensitive substrates/active materials and R2R production.
- Reduce the manufacturing costs by partly or totally replacing silver with copper and/or aluminium.

More specifically, WP1 tasks were focused on the following subjects:

- Design synthesis and characterization of metal nanoparticles (NPs), including silver, copper, and aluminium NPs as metal precursors, and optimization of the synthetic procedures.
- Design synthesis and characterization of silver/copper/aluminium complexes.
- Preliminary ink formulations and optimized formulation of conductive inks for reliable industrial inkjet printing.

Design synthesis and characterization of silver NPs precursors

HUJI precursors

The synthesis was performed in aqueous medium by reduction of the metal salts by a proper reducing agent in the presence of a polymeric stabilizing agent. Since one of the main targets of the project was the formation of stable conductive inks which can be sintered at low temperature, the synthesis was tailored properly. To fabricate precursor with optimal properties, various parameters, such as the reagents concentration, the particles size and the precursor metal loading (metal concentration), type and concentration of stabilizing agent, were evaluated. A typical SEM image of synthesized Ag precursor NPs is presented in Figure 4. As can be seen in the HR-SEM image presented in Figure 4, the size of Ag is in the range of 20-200 nm.

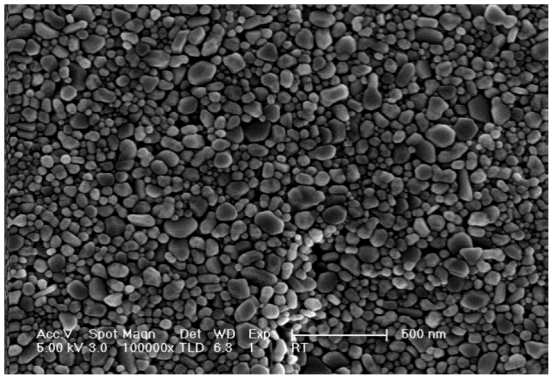

Figure 4: SEM image of Ag precursor NPs obtained by optimized synthetic procedure.

Agfa precursors

From the start of the project, Agfa focused on various concepts, all solvent based. The final concept (Silvidon) was based on first dissolving / dispersing of Ag NPs precursor (like silver oxide) in a specific solvent mixture (major solvent being 2-pyrrolidone) and next reducing at low temperature by a proper reducing agent. It was found that the specific solvent mixture is able to stabilize at high silver concentrations both the precursor silver compound and the final silver NPs. This enables the highly wanted property to avoid polymeric stabilizers, so formation of conductive inks which can be sintered at low temperature became possible.

Many tests were performed to optimize precursors by changing various parameters, such as the reagent concentration, synthesis temperature, solvent mixture, precursor metal loading (metal concentration), type and concentration of reduction agent, additional ingredients and stabilizers, type and preparation of the precursor, etc. After experimental work, finally a precursor synthesis process was worked out to deliver a metal load of approx. 40%, although higher concentrations above 55% are also possible. However, the 40 wt% concentration is ideal for conductivity and formulation of the inkjet inks even if larger amounts of other solvents are added and still allowing 20 wt% silver ink metal loadings. The "Silvidon" precursor is characterized by good shelf life stability.

Design synthesis and characterization of copper NPs precursors

HUJI precursors

The work was focused on the synthesis of air stable Cu NPs precursors. Cu NPs were prepared by reducing Cu salts in water in the presence of a polymeric stabilizer to form dispersions of Cu NPs. The synthesis was optimized in terms of reagent concentrations, reaction temperature and duration, etc. The concentration of Cu at the reaction stage was in the range of 5 to 8 wt%. As seen from Figure 5, the variation in stabilizer concentration enables control of the particle size, and increase in polymer-to-metal weight ratio results in decrease in the particles size.

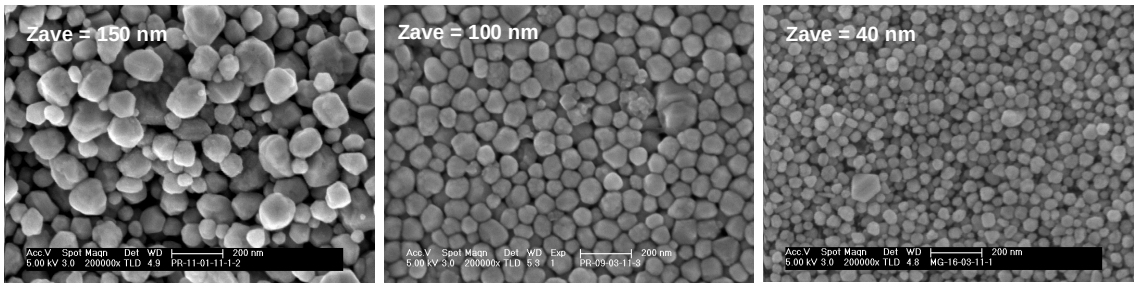

Figure 5: SEM images of Cu nanoparticles synthesized with the use of increasing concentrations of polymeric stabilizer (from left to right).

Since the main challenge in replacing Ag by Cu is avoiding its oxidation at ambient conditions, an effective approach to overcome the oxidation issue is to cover Cu nanoparticles with thin shell of a proper stable and conductive material.

We developed a transmetallation reaction, when the surface of a pre-formed core is sacrificed as a reducing agent for the second metal with higher reduction potential, and the result of such reaction is formation of envelope (shell) of Ag on the top of core Cu NPs.

One more Cu precursor was particulate dispersed insoluble Cu salts obtained by grinding or solvent precipitation.

Design synthesis and characterization of aluminium NPs precursors

HUJI

Commercially available Al NPs were selected as precursors for Al inks. Since such NPs are coated with a thin oxide layer, the research was focused on several approaches to obtain conductive Al ink precursors:

1. Removal of surface oxide layer and preventing oxidation by using organic chelating agent hexafluoroacetylacetone (Hhfa).
2. Removal of surface oxide layer by a proper etching agent (ammonium fluoride, NH_4F, in mixture with strong acid) followed by formation of protective Ag shell on the surface of core Al nanoparticle.
3. Formulation of inks based on dispersion of commercial Al nanoparticles.

Unfortunately, all above approaches did not result in complete removal of oxide layer, and there was still an undesirable amount of oxygen on the surface of Al NPs that makes their use as conductive ink precursors very problematic.

Design synthesis and characterization of silver/copper/aluminium complexes (ICL, TNO, HUJI)

Silver complexes

Promising Ag carboxylate and azodicarboxylate complexes, which decompose in the temperature range of 70-300 °C with formation of metallic silver deposits, were synthesized. Their stability in solution, however, turned out to be insufficient to allow proper ink formulation and processing, as the decomposition started already in the cartridge. Silver complex based conductive inks were therefore abandoned in an early phase of the project.

Copper complexes

Cu(II) azodicarboxylate, Cu(II) hydrazidocarbonate, Cu(II) 2-hydroxyethylhydrazine, Cu formate, and Cu(II) amine complexes which decompose in the temperature range of 130-170 °C with formation of metallic Cu deposits, were synthesized, and their applicability as ink precursors was demonstrated. Especially the formulations based on Cu formate and amino complexes exhibited excellent stabilities and could be conveniently processed by inkjet printing. A major drawback were their rather low copper loads (generally in the order of 12 – 15 wt% or below). Thermal sintering needed to be carried out under protective atmosphere in order to avoid reoxidation and yielded conductivities up to 10 % of the bulk value of copper for drop cast deposits. Such promising values, however, could not be reproduced for printed lines, most probably because the amount of precursor material in these structures was significantly lower than in drop cast samples, giving rise to very thin and rather discontinuous metal deposits. Photonic sintering proved unsuccessful due to the very limited light absorption of the complexes, as compared to layers of metal nanoparticle inks with comparable thicknesses. Further research is necessary to investigate strategies to enhance the absorption and in thus way make photonic sintering more efficient.

Aluminium complexes

Alane complexes with low decomposition temperatures, such as [($EtMe_2N$)AlH_3], [(NMP)AlH_3], [(BH_4)AlH_2(NMe_3)], and [AlH_3($O(C_4H_9)_2$],were synthesized as ink precursors. The compounds were fully characterized, and their thermal decomposition behaviour was studied. All complexes are highly reactive towards even very low amount of oxygen and moisture and therefore need to be prepared, stored and processed under protective atmosphere. The borane and dibutylether complexes decomposed quickly upon storage at room temperature and were found to be unsuited as base materials for functional inks. By contrast, the amino alane complex could be conveniently stored under exclusion of air and water. It was shown that it easily decomposes at moderate temperatures (120°C and below) into conductive aluminium layers, a reaction which takes place at even lower temperatures (80 – 100°C) in the presence of titanium complex catalysts. Due to the intrinsic environmental sensitivity of this material and the early phase in which this research still is, no printing experiments could be carried out with it. Instead, printing of the titanium complexes and subsequent selective deposition of aluminium through the vapour phase at atmospheric pressure was demonstrated. In a similar fashion, homogenous coatings of aluminium grown on substrates pretreated with titanium complex were obtained with conductivities up to 50 % of the bulk Al value.

Preliminary ink formulations and optimized formulation of conductive inks for reliable industrial inkjet printing

Table 1 below presents progress in ink formulations developed during the project performance.

Table 1: Overview of the most important ink formulations prepared and tested in the course of the LOTUS project

Ink	Precursor type and concentration	Carrier (solvent)	Sintering temperature (°C)	Comments
HUJI-001	Al NPs, 10 wt%	Organic solvent	>600	Not printable, bar coating on glass
HUJI-002	Ag NPs, 20 wt%	Water	>200	
HUJI-003	Cu@Ag (core/shell) NPs, 20 wt%	Water	>200	
HUJI-004	Ag NPs, 20 wt%	Water	>200	
HUJI-005	Ag NPs, 30 wt%	Organic solvent	~190	Conductivity 20% of bulk Ag
HUJI-006	Ag NPs, 50 wt%	Organic solvent	~200	Conductivity 25% of bulk Ag
HUJI-061	Mixture of Ag nanoparticles of HUJI (25 wt%) and Imperial Ag organometallic compound	Organic solvent	120	Not printable (low stability)
HUJI-007	Cu NPs, 30 wt%	Organic solvent	>200	Conductivity 7% of bulk Cu
HUJI-010	Ag NPs, 30 wt%	Organic solvent	~150	Sheet resistance <1 Ω/□
HUJI-011	Cu NPs, 50 wt%	Organic solvent	~170	
HUJI-012	Cu organometallic complex, 15 wt%	Organic solvent	<150	Paste
HUJI-014	Cu organometallic complex, 12 wt%	Organic solvent	<150	Sheet resistance 0.035 Ω/□
HUJI-015	Cu NPs, 35%	Organic solvent	<200	Up to 15 % of bulk Cu by photonic sintering on glass
HUJI-016	Ag NPs, 30 wt%	Organic solvent	120	Sheet resistance 0.1 Ω/□
HUJI-017	Ag NPs, 50 wt%	Organic solvent	120	Sheet resistance

				0.1 Ω/□
HUJI-018	Cu organometallic complex, 8 wt%	Organic solvent	<170	Inkjet printable
Agfa "Zilcon"	Ag NPs,	Organic solvent	250 170	Conductivity 50% of bulk Ag 10% of bulk Ag Bad jettability
Agfa "Silvaca/Silvoxa"	Ag NPs, 30 wt%	Organic solvent	140 <170 250-220	Conductivity <%1 of bulk Ag 11% of bulk Ag 30% of bulk Ag Coffee stain effect
Agfa "Silvedot"	Ag NPs in combination with conductive polymer PEDOT/PSS		250	>25% of bulk Ag Coffee stain effect
Agfa "Silbimin"	Ag NPs,	Organic solvent	130	>10% of bulk Ag (blade coating) Plate wetting with Dimatix printing
Silvidon 3422420 (T6)	Ag NPs, 20wt%	Organic solvent	150 130	Conductivity 34% of bulk Ag 14% of bulk Ag
Silvidon 3420337 (T4)	Ag NPs, 20 wt%	Organic solvent	150 130	Conductivity 34% of bulk Ag 14% of bulk Ag
Silvidon 3426508 (T5)	Ag NPs, 23 wt%	Organic solvent	150	Conductivity 54% of bulk Ag
Silvidon 3421392 (T6)	Ag NPs, 39 wt%	Organic solvent	150	Conductivity 32% of bulk Ag
Imperial	Azidicarboxylate complex of Ag	Organic solvent	Flash sintering	<1% of bulk Ag
Imperial	$AgNO_3$ + acetone semicarbazone, Ag loading 7.19 wt%	Organic solvent	160	Sheet resistance 0.0755 Ω/□
Imperial	Cu formate, 2 wt% of Cu	Organic solvent		No printing experiments, only drops deposition
ICL-Cu-2A	Cu formate/ethanol amine/ethylene glycol	Organic solvent	110-200	Drop casting
ICL-Cu-2B	Cu formate/hexylamine	Organic solvent	110-200	Drop casting
ICL-Cu-2C	Cu formate/*n*-butyl amine	Organic solvent	110-120	Drop casting
TNO-Al-2A	N,N-dimethylethylamine alane	No solvent, 26 wt% Al	100	CVD type process, decomposition supported by Ti catalyst; up to 50% of bulk Al conductivity
TNO-Al-2B	N,N-	Organic solvent,	100	CVD type

	dimethylethylamine alane	1.6 wt% Al		process, decomposition supported by Ti catalyst; up to 50 % of bulk Al conductivity
TNO-Al-3	Borane amino alane	No solvent, 26 wt% Al	Not tested	Instable at room temperature
TNO-Al-4	dibuthyl ether alane	No solvent, 17 wt% Al	Not tested	Instable at room temperature

To date, four Ag-based ink formulations (HUJI-010, HUJI-016, HUJI-017) and Agfa Silvidon inks 3420337, 3426508, 3421392, and 3422420 enable obtaining printed pattern with high conductivity at low sintering temperatures, not higher than 150°C. These inks can be used for fabrication of the demonstrators.
Cu organometallic ink HUJI-018 with metal loading of 8 wt%, which is characterized by optimal printing performance, can also be recommended for inkjet printing of demonstrators.

The main dissemination activities
HUJI: 6 articles, 6 reviews and book chapters, 4 patent applications, 19 conference presentations.
ICL: 1 article, 2 conference presentations
AGFA: 4 patent applications

Exploitation results
Personnel: 6 qualified specialists in the field of conductive nanomaterials, inkjet printing and sintering methods were trained.

Main results of WP 2

Introduction

The key processing aspects crucial for the low cost high throughput production of conductive lines for Printed Electronics applications are a fast, precise and highly reliable deposition process, and a very efficient sintering process operating at low temperatures. Only when these requirements are fully met will it be possible to apply R2R manufacturing at economically viable process speeds using inexpensive substrates, such as commodity polymer foils or paper, which are generally rather heat sensitive.

The goal of the LOTUS project was to approach these technical challenges in a concerted and coordinated manner by engaging representatives from the entire value chain, starting from ink manufacturers, via process developers to end users, since a successful technology process development will require intense interaction between all involved parties. A detailed theoretical understanding of the underlying physics is also expected to strongly support the practical applied research activities. Consequently, within the LOTUS project, WP2 (Processing), bridges the gap between WP1 (Ink Development) and WP4 (Integration, Assessment), with WP3 (Specifications, Modelling) also heavily relying on its experimental input, for model development and calibration as well as validation.

Key results of WP2

Printing technology

In the project description, inkjet printing was defined as the sole deposition technology to be explored within the framework of the LOTUS research. Since it is a well-established technology in industrial production processes, especially for graphic and decorative applications, no research needed to be carried out to further explore and develop this technique on a fundamental level. One main objective of WP2 was therefore to optimise the inkjet process for the formulations developed in WP1 with their specific physical properties, and to enable up-scaling for pre-pilot R2R application.

In order to support Hebrew University, Imperial College and Agfa in their ink development activities, a standardised test procedure was defined, consisting of the characterisation of the supplied formulations' jetting behaviour and interactions with a number of technologically relevant substrate surfaces. Since WP1 delivered an impressive amount of samples to test, the first screening was carried out on small scale, using a commercially available materials printer. The big advantage of this approach is that a large number of candidates could be tested without the need for large amounts of sample material (typically 5 – 10 ml of ink was sufficient for a full characterisation), and that the procedure was not too time consuming, but still allowed a good estimation which inks would deserve a more detailed investigation on larger scale. Optimised printing conditions were determined by variation of jetting and non-jetting waveforms, drop ejection frequency and nozzle temperature. Important criteria for satisfactory printing performance were the reliability and stability of the jetting process, the number of functioning nozzles, the straightness of the jets, the amount of satellite formation, and the shelf-life of the cartridges.

A second criterion of equally high importance for judging a formulation's suitability for industrial application was how it interacted with a number of substrates which will be used for the envisioned applications. These included a number of bare and coated plastic foils, as well as glass for reference reasons. Depending on the ink's and substrate material's surface properties, the spreading behaviour of the ink upon impact of the droplet will determine whether well-defined structures with high resolution can be formed. In the case of inadequate interactions, either strong spreading will occur and very shallow and broad lines with ill-defined edges be formed, or dewetting will result in isolated droplets instead of continuous lines. Measures taken to improve the wetting behaviour were variation of the substrate temperature and amount of deposited ink, changing of the substrate's surface energy by plasma treatment, or adjustments to the ink formulation.

Additional characteristics tested were the surface profiles of the inks upon drying and sintering (vide infra), and their adhesion to the substrates under investigation, which is important for implementation in functional devices.

The results from these tests were reported to the respective ink suppliers, together with suggestions on how to adapt the composition of their products in order to improve their performance.

A selected example of a well-behaving ink formulation is visualised in Figure 6.

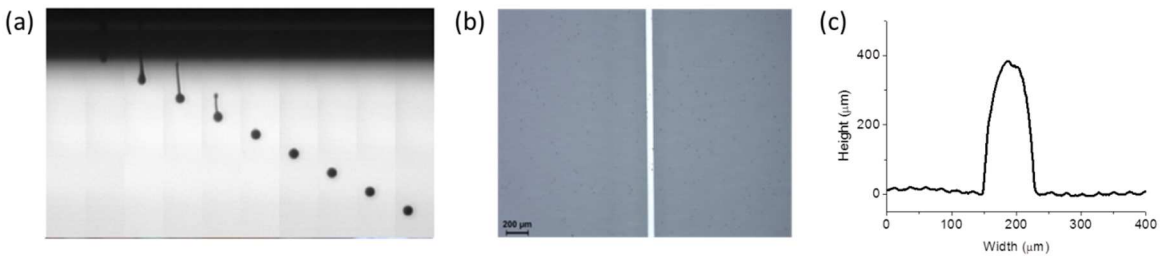

Figure 6: Jetting behaviour (a), line definition (b) and height profile (c) of a conductive ink.

After this selection process had been finished, one formulation based on a silver nanoparticle dispersion was chosen as the most promising candidate to apply on larger scale. It was subjected to a more detailed testing and optimisation procedure, which required larger volumes of ink (in the order of 50 ml) and involved also the use of industrially relevant inkjet heads with large amounts of nozzles (a few hundreds up to one thousand). Essentially, the entire process described above was repeated under these conditions which more closely resembled those common in manufacturing on an industrial scale. The optimised printing parameters obtained in this way served as starting point for testing the formulation on an even larger scale using a R2R compatible equipment.

In contrast to the equipment used for the testing on small and medium scale described above, there was no industrial inkjet tool available directly suited for the printing of conductive inks on such large scale. It therefore had to be specifically designed and constructed by the LOTUS consortium partner Xennia, and was installed on the R2R processing line present in Holst Centre's laboratories. This design and construction included the print system (printheads, print software and recirculating ink system; see Figure 7 and Figure 8).

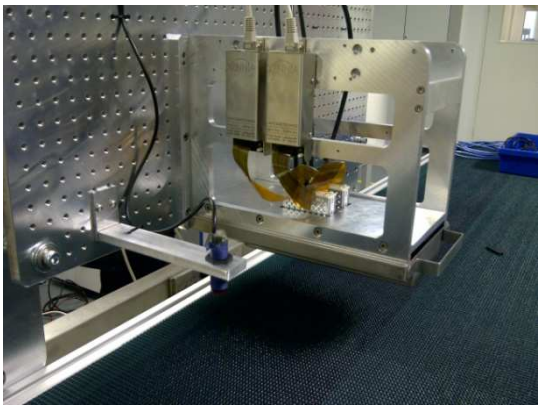

Figure 7: LOTUS Printhead module

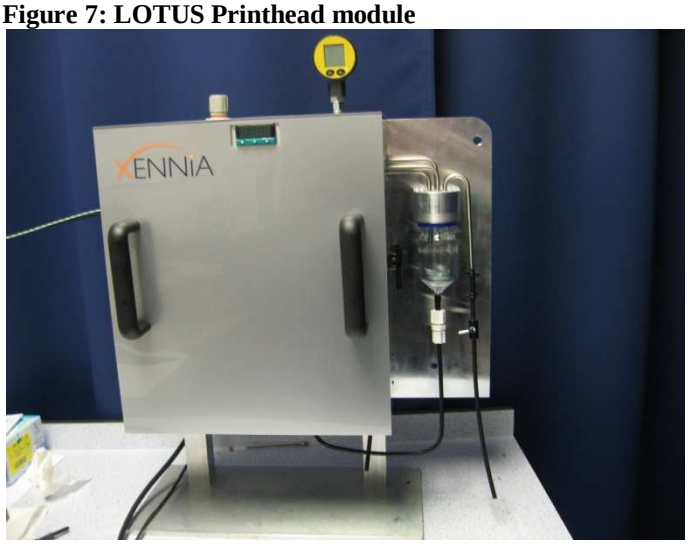

Figure 8: LOTUS Small volume Ink Management System (SIMS)

In order to achieve the required high resolution parallel and orthogonal to the printing direction, two inkjet heads were installed next to each other. The necessary adjustments such as head alignment and synchronisation, needed to be done using a commercially available conductive ink, since WP1 was at that moment not yet able to supply a suitable

formulation in the required quantities (a few hundreds of ml). After the synthesis of the silver particles and the formulation had been successfully scaled up, the R2R printer was switched to the LOTUS material. After another round of printing condition optimisation, based on the parameters obtained from the smaller scale experiments, the process was stable enough to allow the continuous printing of functional silver patterns on several hundred metres of foil with substrate speeds of up to 20 m/min.

Sintering technology

In parallel with testing the printing performance of the formulations provided by WP1, also their sintering behaviour needed to be studied, since achieving high conductivities (at least 20 % of the bulk silver value) at high processing speeds (in the order of a few seconds or faster) and low temperatures (below the deformation point of the used substrates) is crucial for a successful application in a R2R process. Only those formulations developed in WP1 which exhibited promising printing behaviour and ink-substrate interactions were extensively tested with respect to their sintering characteristics. Feedback about sintering speed, achieved conductivities and suggested improvements was provided to the suppliers which enabled them to adjust their formulations.

In contrast to the deposition technique, which had been predetermined during the planning of the project, several alternative sintering technologies had been chosen to be investigated for their compatibility with R2R manufacturing. The conventional approach of thermal sintering by prolonged exposure to elevated temperatures was included as a baseline process, against which the alternatives were benchmarked. In the course of the project, the most promising technology was selected for application on a larger scale on the R2R pre-pilot line in combination with the Xennia printer.

Hebrew University developed a chemical sintering approach based on a specific interaction between the polymer used to stabilised their silver nanoparticles and a sintering agent either added to ink formulation or applied after the deposition process. The details of this technique are described in WP1, but its core advantage from a processing point of view is that it occurred without any temperature increase and is therefore compatible with almost any type of plastic substrate. Up to 25% of the bulk silver conductivity have been achieved within very short processing times, but for application on a large scale, the technology was not yet mature enough.

Exposure of the printed ink structures to plasmas either created at low or atmospheric pressures was investigated by Jena University, the alternative at ambient conditions being the more attractive approach for industrial application from a practical point of view. The proposed mechanism is the partial decomposition and removal of the isolating polymer shells added to prevent nanoparticle agglomeration in the ink. This results in destabilisation of the highly reactive metal surfaces which consequently coalescence spontaneously. Although plasma sintering does not involve direct heating, usually some temperature increase was observed, which was more pronounced at longer exposure times. The peak temperatures, however, tended to remain limited (i. e. below 100°C), which is acceptable for almost all relevant polymer foils. Conductivities exceeding 50 % of the bulk silver value have been achieved with certain types of inks, but generally the long processing times were found to pose so serious challenges for possible R2R applications that it was decided not to scale up plasma sintering within the scope of LOTUS.

Rather than relying on chemical reactions to trigger sintering, as in the case of sintering agents and plasma exposure, selective heating of the ink layers can be a promising alternative to indiscriminative heating of both ink and foil, as is with thermal sintering. Jena University has used microwave radiation to dissipate energy directly in ink structures which already exhibited a limited conductivity, with the result of very localised heat development only within the metal. Very short processing times (in the order of 1 second) and excellent conductivities (up to 46 % of the bulk silver value) clearly demonstrated the potential of this technology, especially since its applicability not only to single isolated lines, but also to functional structures has been shown. In the course of the project, however, the technique turned out not to be sufficiently mature to be further developed and transferred to R2R manufacturing.

Table 2 summarizes the obtained conductivity values for a number of LOTUS inks and sintering techniques.

Table 2: Maximum conductivities for each ink and sintering technique in comparison to bulk metal.

	Silver inks						Copper inks	
	HUJI-002	HUJI-004	HUJI-005	HUJI-006	AGFA	Commercial	HUJI-007	ICL-MH
Low p plasma	11%	6%	10%	27%	40%	12%	2%	0.6%
Atm. p plasma	--	--	12%	--	5%	7%	--	--
Microwave	7%	60%	46%	25%	5%	5-40%	5 Ω/mm	--
Thermal	>60%	>60%	>60%	>60%	39%	50%	10-30%	10%

Figure 9 visualises the concepts used for each of the three sintering technologies discussed so far.

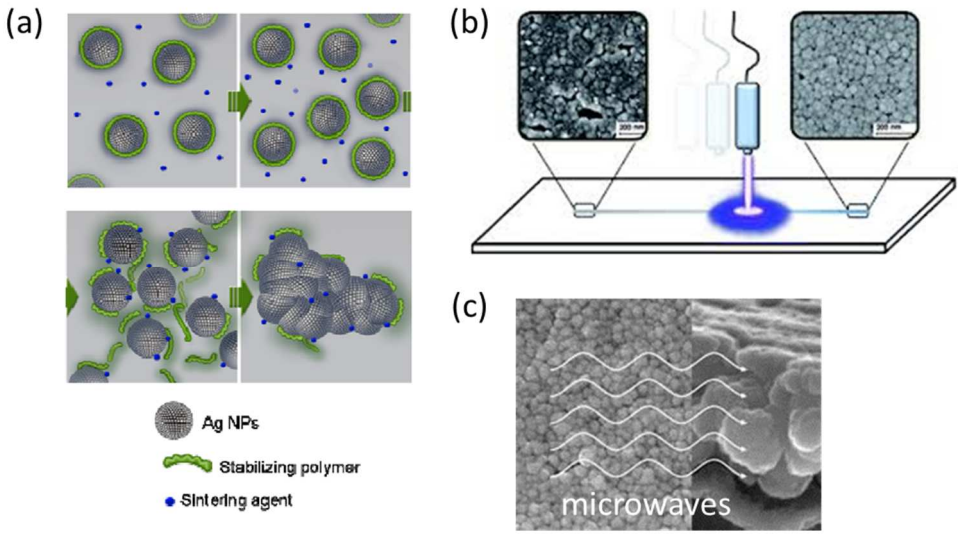

Figure 9: Principle of chemical (a), plasma (b) and microwave (c) sintering.

Another alternative which allows selective heating of the ink and not the foil is the illumination with visible light instead of microwaves, the so-called photonic sintering approach. It has the decisive advantage that it also works for initially non-conductive ink structures, as long as the difference between the absorption spectra of ink and foil differ sufficiently and a lamp with appropriate emission characteristics is used. Applying the light in highly intense, but very short pulses allows to largely suppress heat transfer into the substrate and to confine the peak temperatures to the ink layers and their immediate surroundings, which limits foil deformation. Based on this approach, Holst Centre has designed and constructed a number of photonic sintering tools, which, in parallel with the strategy described for the ink benchmarking, allow to study and optimise the process at different scales, ranging from simple single lines to A4 sized functional patterns. Except for in-line resistance measurement, also the temperature can be monitored during illumination, allowing a detailed process study of parameters such as the line dimensions, pulse energies and lengths, and flashing frequencies. With a number of LOTUS silver inks, conductivities up to 28 % of the bulk silver value could be obtained within fractions of a second. At the same time, foil deformation remained limited due to the short process times. Copper nanoparticle based inks turned out to be more difficult to sinter photonically, requiring much higher processing temperature or longer exposure to the radiation. This made necessary the use of either more powerful lamps or inert

atmosphere and high temperature stable substrates. Finally, conductivities up to 15 % of the bulk copper value were achieved.

Due to its promising results on small and medium scale, it was decided to also investigate the potential of photonic flash sintering on a R2R basis. For this purpose, Holst Centre constructed a R2R compatible sintering unit which was mounted on the pre-pilot production line with the Xennia inkjet printer. After the necessary optimisation work, the LOTUS consortium succeeded in producing structures with lines as narrow as 40 micron and conductivities up to 15 % of the bulk value at line speeds of 4 m/min. The applicability of this combination of processing technologies for the R2R manufacturing of functional structures for the Printed Electronics industry was demonstrated by producing several hundred metres of RFID antennas at 20 m/min, which were provided to smartrac for device integration.

Figure 10 shows experimental results for photonic sintering and the R2R line used to demonstrate pre-pilot production.

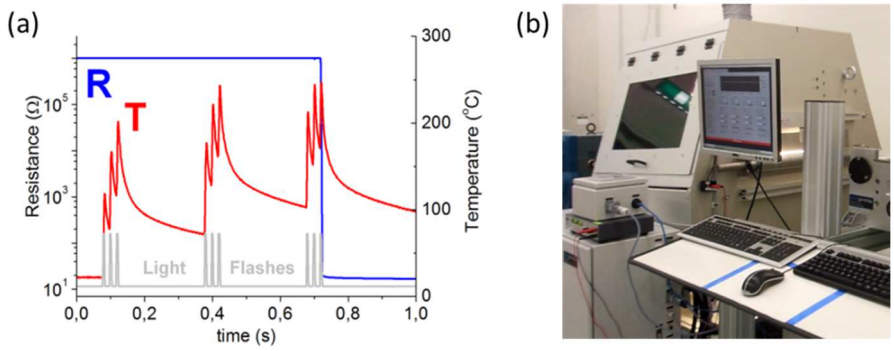

Figure 10: Resistance and temperature in a printed line of a silver ink during photonic flash sintering (a). R2R photonic flash sintering unit (b).

Summary and Conclusions

Within the framework of the LOTUS project, the participants of WP2 have intensely interacted with the ink suppliers (WP1), as well as with the end users (represented in WP4 and WP5). A benchmarking process has been developed allowing WP1 to continuously improve the printing and sintering performance of their inks. Several sintering mechanisms for conductive silver inks were experimentally compared for their application potential in R2R manufacturing, and photonic flash sintering was selected as the most promising approach. A R2R line with a specifically designed inkjet printing and sintering unit has been constructed and its practical applicability for the Printed Electronics industry was demonstrated using an ink formulation developed within the LOTUS project.

Main results of WP3

Within this work package, a simulation model for the ink-jet printing process was developed. The model consists of two parts: (1) a macroscopic drying model, which predicts the flow field inside the droplet, and (2) a microscopic Brownian Dynamics model for the individual solid particles. By coupling these two models, a simulation program was set up where the trajectory of each particle inside the droplet is calculated based on Brownian motion, the flow field, inter-particle forces and boundary conditions. The initial particle positions within an ink-drop and a flow field during drying are shown in Figure 11.

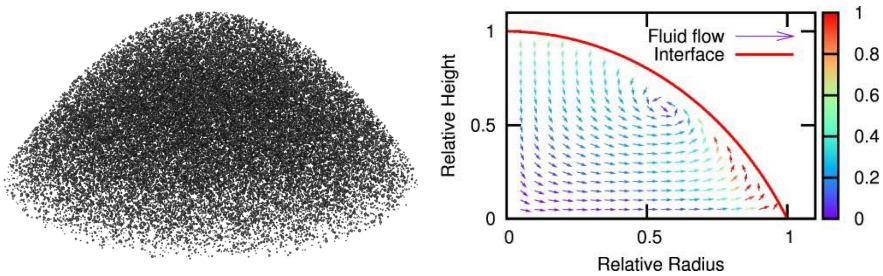

Figure 11: Initial particle positions within an ink-drop and a flow field during drying.

The simulation model has been validated against experimental results by Shen et al. [1], finding very good agreement between theory, experiment and simulation results. This can be seen from Figure 12, which shows a comparison of experimentally dried droplets and the according simulation results.

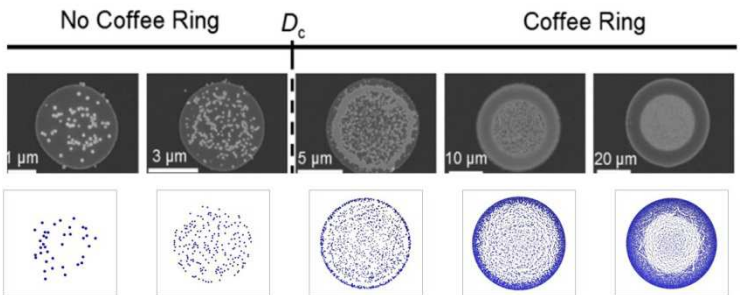

Figure 12: A comparison of experimentally dried droplets (top) [1] and the according simulation results (bottom).

The model was then used to carry out parametric studies in order to investigate the influence of both process and ink parameters. In depth investigations where performed for the influence of the drying time, the wetting regime (i.e. contact angle), the solid content of the ink, the particle size distribution as well as the influence of different atomistic forces models and boundary conditions. The model has also been applied to investigate for a specific ink the transition between ring formation during drying and a fully covered substrate. For more detailed information the reader may refer to the previous reports, where extensive information about the simulation model, results and conclusions has been reported.

Both, progress in modelling and the simulation results where periodically presented to and discussed with the project consortium. In addition, the simulation model, its validation as well as the most important results are currently being published in a scientific journal [2].

[1] X. Shen, C.-M. Ho, T.-S. Wong, Minimal size of coffee ring structures, J Phys Chem B 114 (16) 5269-5274, 2010.

[2] T. Breinlinger, T. Kraft, A simple method for simulating the coffee stain effect, Powder Technology, 2013 (submitted)

Modelling and simulation of the metal nanoparticles sintering process (FhG)

Within this task, a simple phenomenological sintering model for the computation of resistivity evolution during sintering has been developed. It splits into two stages: In stage 1, the sintering process of the line is simulated with a particle-based discrete element method (DEM) that allows tracking the particle positions during sintering including rearrangement and contact formation of each particle. In stage two, the resistivity is computed with the help of specific parameters that can be extracted from the process simulation of stage 1.

The process simulation method (stage 1) is based on an existing model for sintering on the particle-scale and is explained in more detail in Deliverables 3.5 and 3.6. A consideration of a core/shell topology that was planned at the beginning of the project has been discarded because of experimental findings that revealed only a minor correlation between residual organic content in the printed line and resistivity changes (see WP2 Task 6 in this report). To account for the existence of organic matter that initially prevents particles from touching each other and therefore delays conductivity in the line, a heuristic parameter was introduced that reproduces this behaviour and was to be fit to experimental data. The model was applied to particle assemblies with free top surface, constraining substrate at the bottom and periodic boundary conditions in plane-direction mimicking an infinite thin film with an initial thickness h_0, which is in accord with experimental measurements for ink-jet printed lines. This assumption is justified by the fact that length and width of the ink-jet printed line exceed line height by far. A typical particle assembly used for simulations is shown in Figure 13**a**.

A free parameter contained in the process simulation method has been fit to experimental data for isothermal sintering of a silver ink at 175°C obtained within WP2 by FSU. This silver ink (HUJI-005) was produced within WP1 by HUJI. Subsequently, simulations have been performed and compared with experiments at other temperatures with regard to line height loss in order to validate the model. The result is displayed in Figure 13**b**, revealing good accordance for 150°C but a remarkable discrepancy for 200°C, for which experimental data shows hardly any difference to the case of 175°C.

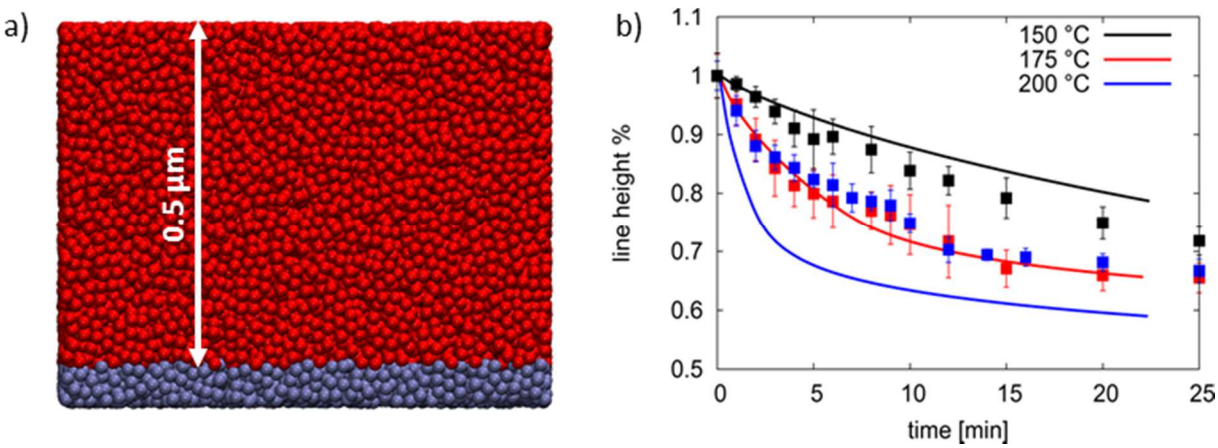

Figure 13: Assembly used for simulations consisting 38.000 particles (a); simulated (lines) and measured (dots) line height decrease during sintering of an inkjet-printed line. A free simulation parameter was fit according to the experimental data for 175°C (red).

In stage 2, the resistivity is computed with the help of specific parameters that can be extracted from the process simulation of stage 1: the average coordination number k, the average contact radius c, the percolation time t_0 (the point in time at which for the first time a path of connected particles passes through the simulation sample) and a parameter μ representing the topology of all percolation paths. These values were inserted to an equation that calculates resistivity ρ as a function of time:

$$\rho = \begin{cases} \infty & , \ t < t_0 \\ \rho_{bulk} \left(a_1 \cdot \exp\left(a_2 \cdot \frac{\lambda}{k \cdot c \cdot \mu} \right) + a_3 \right) \frac{h}{h_0} & , \ t \geq t_0 \end{cases}$$

The derivation of this equation can be found in deliverable 3.6.

The calibration of the model via the free parameters a_1, a_2, a_3 as well as the validation was achieved again with the help of data from the accompanying experiments at different isothermal temperatures. The results can be found in Figure 14, showing a good agreement regarding the starting time of non-infinite resistivity and the gradation of the final resistivities, i.e. a higher sintering temperature leads to lower the final resistivity.

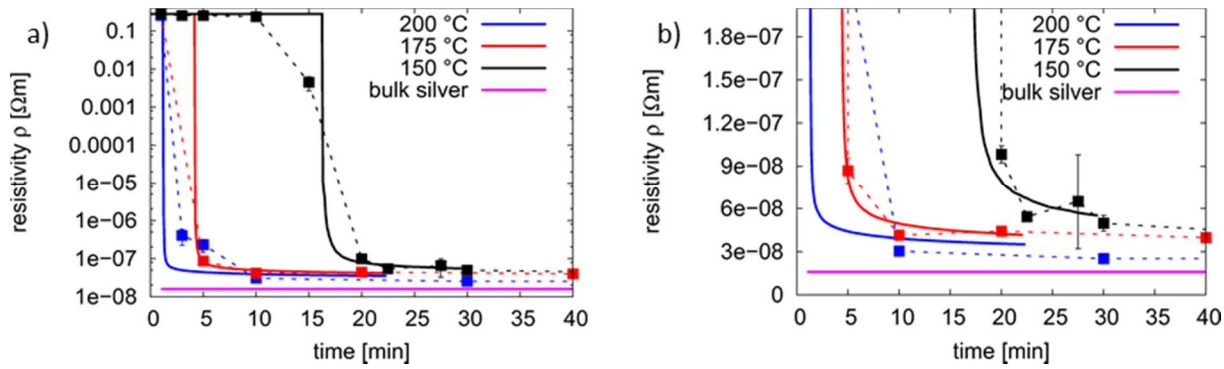

Figure 14: Comparison of resistivity measured in experiment (dots) and computed by (solid lines) with parameters fitted to data for 175°C with logarithmic scaling (a) and unscaled in the range of interest (b)

After validating the model, the influence of particle size and size distribution on resistivity evolution during thermal sintering has been investigated. Figure 15**a** shows the resistivity evolution for samples consisting of particles with various sizes. Apparently, particle size affects remarkably the percolation time at which a finite resistivity can be measured for the first time. The reason for this is the sintering delay for larger particles - an effect that is well known. Moreover, Figure 15**b** reveals that also the final resistivity increases with increasing particle size, at least in the investigated time range.

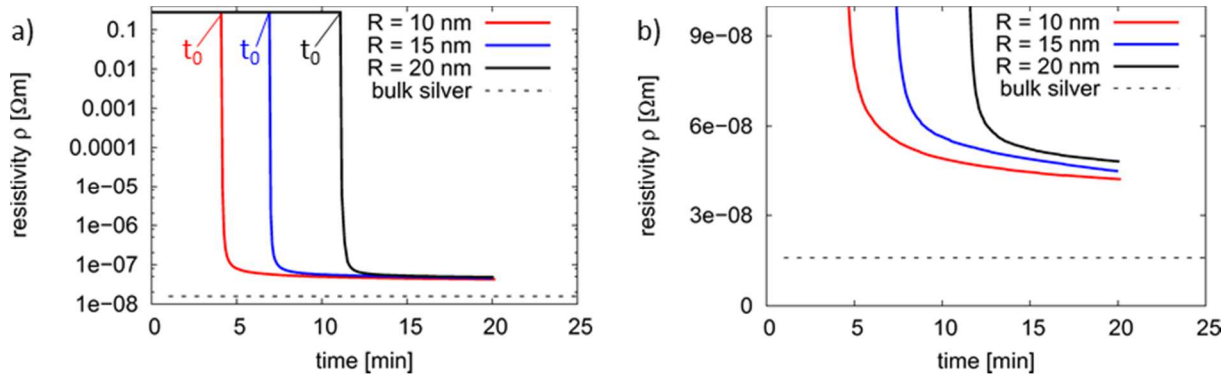

Figure 15: Computed resistivities for printed lines composed of particles with different sizes with logarithmic scaling (a) and unscaled in the range of interest (b).

In order to analyse the influence of a particle size distribution on resistivity development, samples with equally sized particles of radius r = 10 nm were compared with samples that consist of particles with log-normal distributed sizes (mean radius 10 nm, standard deviations of σ = 0.1 and σ = 0.2, distributions see inset of Figure 16**a**). Since the mean radius is equal within this variation, the starting times of resistivity coincide as shown in Figure 16**b**. The minimum lengths of percolation paths, however, are the lower the broader the particle size distribution is. The reason for this is that

in this case a certain amount of large particles are available that can form a connected particle chain through the sample that is shorter than in the case of narrow particle size distributions. This effect is reflected in the resistivity evolution shown in figure 4b, where a slight tendency to smaller resistivity values for higher σ due to shorter percolation paths is visible.

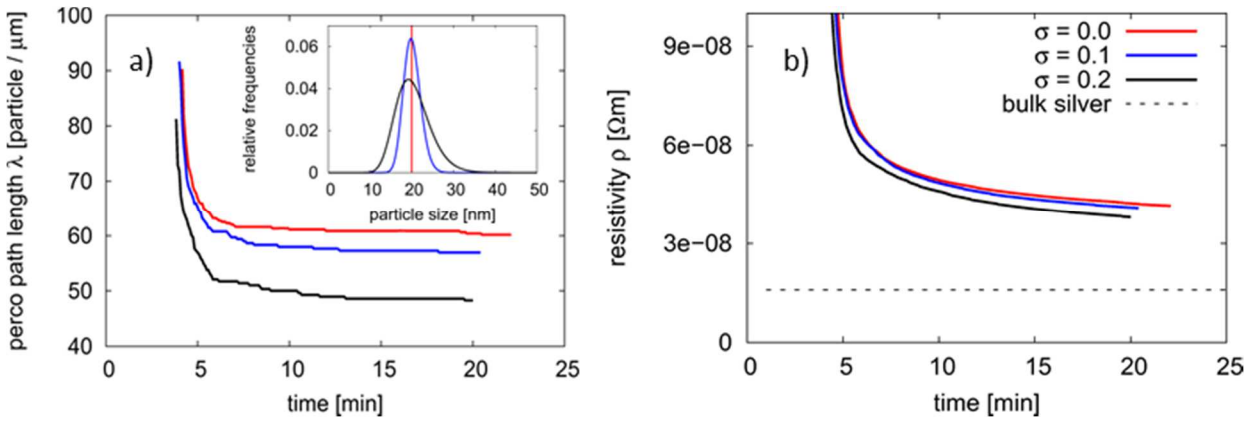

Figure 16: Minimum length of percolation paths for samples with different particle size distributions (inset) (a) and resistivity evolution of these setups (b).

Concluding, parameter variations show that using small particles with a broad particle size distribution and high sintering temperatures are in general beneficial in order to get low resistivity. On the other hand, however, it was shown that even for the best conditions available, it seems not to be possible to obtain feasible resistivity values within a few seconds with thermal sintering which is the goal of this project. The results of this study on thermal sintering are going to be published in a scientific journal in collaboration with FSU and HUJI.

After applying the model successfully to thermal sintering, an attempt has been made to transfer it to photonic sintering by introducing a real temperature profile recorded during experiments at Holst Centre within WP2 as input for the sintering model (see Figure 17**a**). The simulation result is given in Figure 17**b** together with an estimate for the resistivity evolution in experiment. A rather large gap between the starting times at which resistivity becomes non-infinite can be observed as well as a certain discrepancy between the final resistivity plateaus.

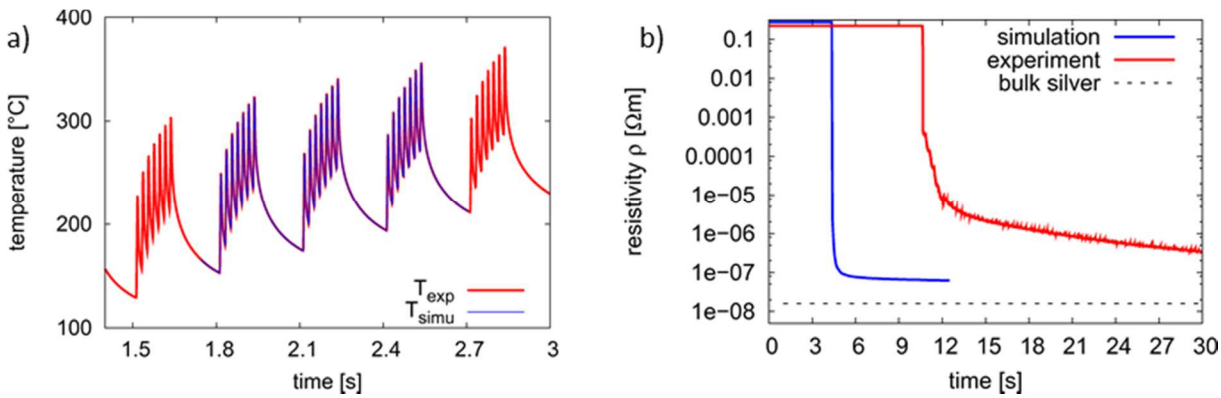

Figure 17: Temperature profile measured during photonic sintering experiments and replication for simulations (a) and corresponding resistivity evolution (b)

Possible reasons for this deviance have been detected (see Annual Report 2013) and further collaborations with Holst Centre beyond the period of this project are planned with the intention to analyse the cause of these discrepancies.

Main results of WP4

Printing for PV was 4 years ago the sole domain of screen-printing. Today conductive inkjet printing is considered an alternative, especially when small device structures are needed. The low conductivity and high costs of the inks posed the two main problems. The use of nano particle inks and smaller cells solved the first but the high costs remain an issue. The smaller printable details, more efficient material use and the low curing temperatures enabled the use of inkjet for all thin film solar families, including organic PV. The non structured large area coating is essential to come to low cost - high volume production of solar foil. The use of inkjet makes it possible to place the serialization of solar cells (needed to keep the current losses low) after all coating steps and avoid in this way alignment, contamination and patterned printing.

This back end serialization route creates a new intermediate product, the uniform solar foil. These foils are used by module makers to produce their solar modules. In combination with the subtractive technology of laser scribing, the additive technology of inkjet enables this new development.

Model, LCA and solar structures for inkjet.

Interconnection model.

The model that was setup during the project is used to calculate the optimal cell sizes and reduced finger structures. The final outcome of mini cells with a reduced finger length proved to minimize also the metal consumption by half compared to the standard method.

LCA

The LCA analyze of the inks showed an improvement due to the reduced thermal load. But the amount of energy needed for the silver metallization is only about 6 % of the total amount of energy needed to build a silicon thin film solar cell. More than 50% is needed for the framing, encapsulation and the substrate (steel). A reduction will made some impact but not much.

Solar structures for inkjet

The inkjet route made new solar structures possible. The simultaneous print of the front and back electrode is for example an important step because this enables a full inkjet printing of the electrode and eliminates alignment of the front and back electrode.

Figure 18: Maple leaf Organic PV solar cells. Front and back electrode Ag inkjet print. Leaf ~ 35 mm. First example of backend OPV connection. (OPV on glass 140 x 140 mm)

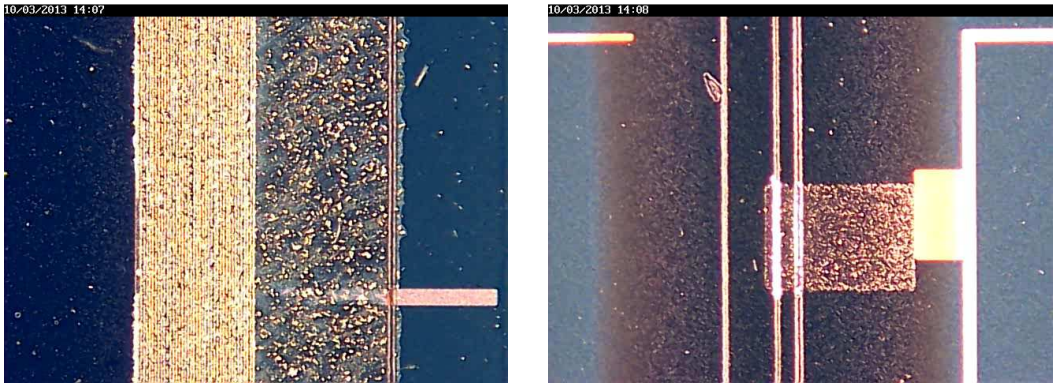

Figure 19: Close up of CIGS solar module. Left: Ag print contact to front electrode (P2). Right: Ag contact pad connection of finger pattern to front electrode (P2)

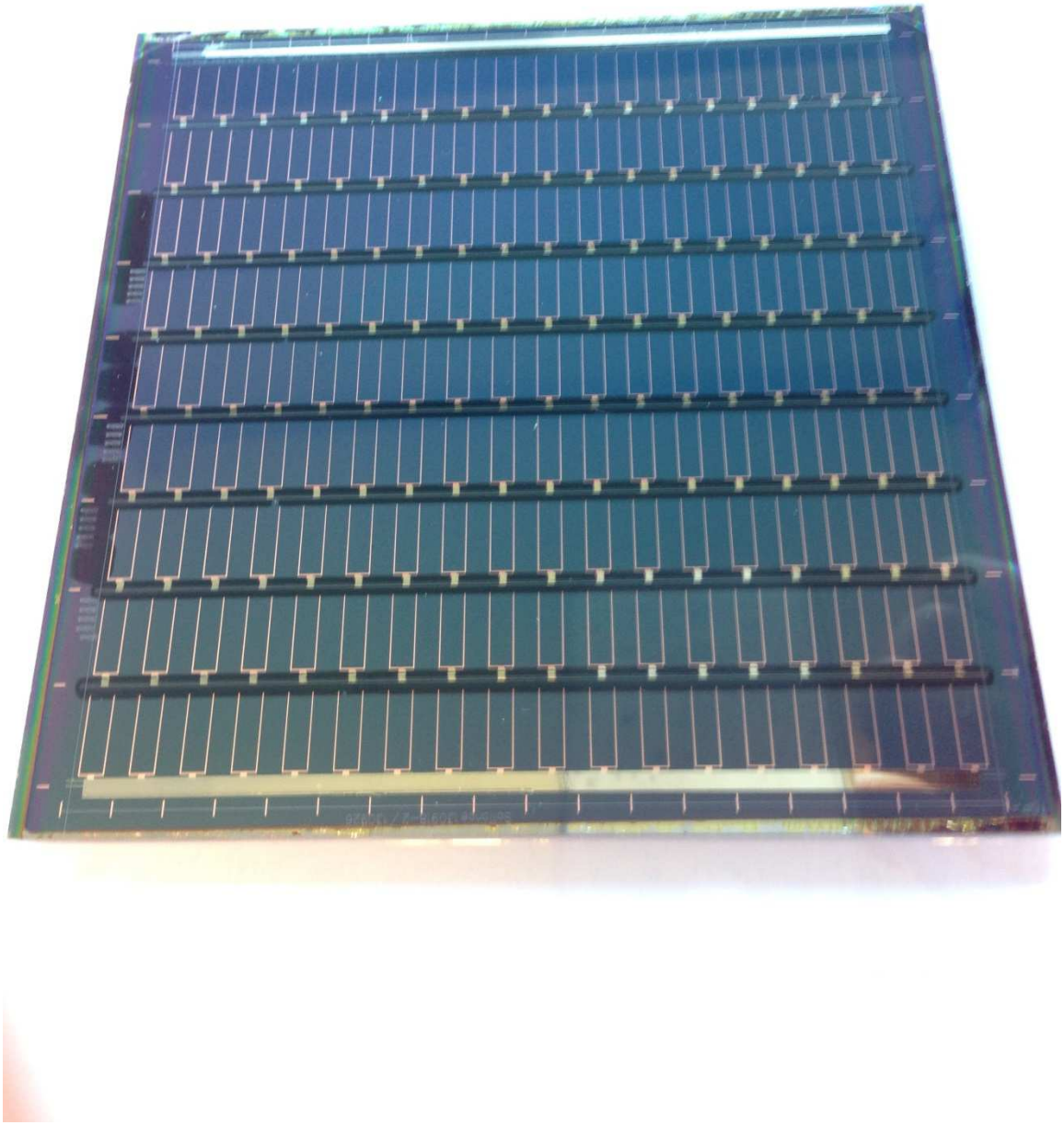

Figure 20: 100 x 100 mm, Cigs (copper indium gallium selenide) module with Isolation inkjet print and Ag contact bars and connections. Used finger pattern is copper due to the available CIGS samples. (CIGS on glass 100 x 100 mm)

Laser sintering

The use of continuous fiber laser opened a route to more localized heating. The test system was built from standard elements and showed similar results as photonic sintering without the need for a transparent substrate avoiding unnecessary substrate heating.

The potential impact

The interconnection being an essential step to create efficient solar cells through higher voltage and low current is brought with the combination of laser (subtractive) and conductive inkjet closer to the module makers. The flexibility of both technologies opens the route to design modules and adapted structures. The building integrated photovoltaic (BIPV) will benefit from this development. It is also the route to bring the solar market closer to its end customers. The high volume production of solar film will become a web-coating domain. The added value will shift more to BIPV suppliers with a good knowledge of the glass market. The costs price of the nano ink will have to drop to the level of screen print ink because an optimized rotational screen printing would be more economical although less flexible and less efficient.

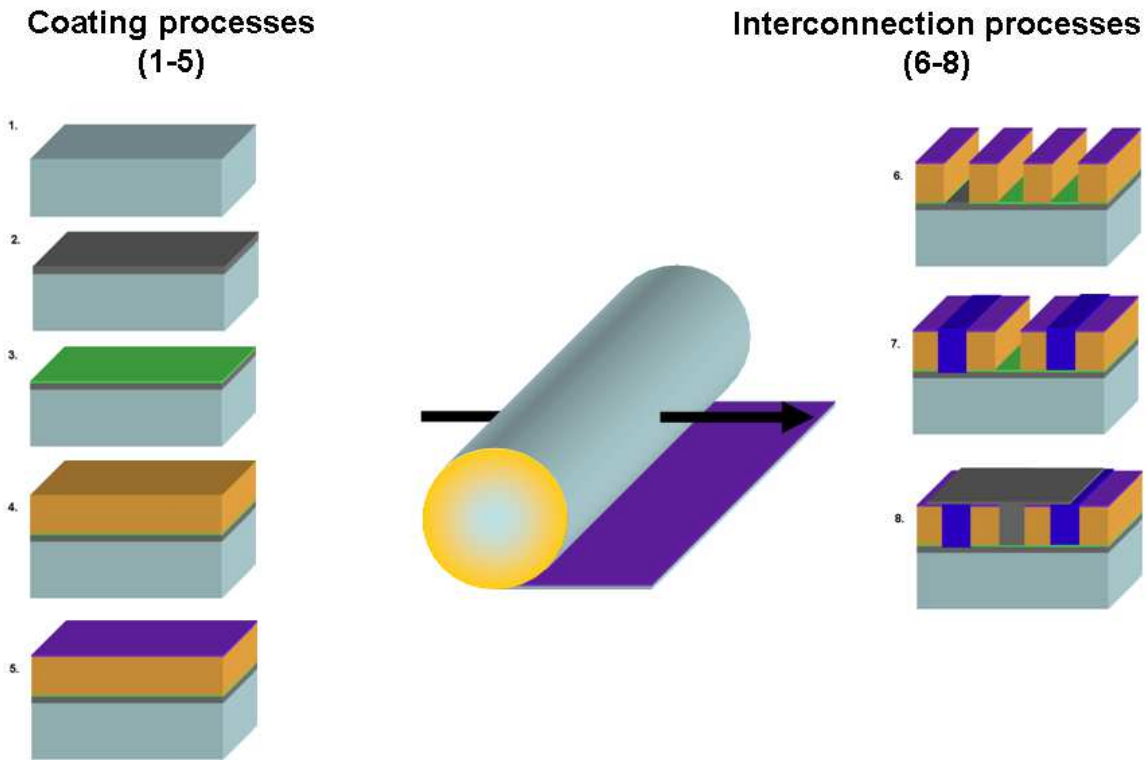

Figure 21: Schematic layout of back interconnection.
Left: Coating processes unstructured. Right: Laser structuring and inkjet printing.

Main results of WP5

Task 1: OLED lighting device demonstrator

HOLST optimised the printing and photonic sintering conditions for HUJI 16, as described in WP2, sections 1.1, 1.3 and 2, and the ink was used to produce an OLED demonstrator device. Since neither the printing accuracy nor the electrical conductivities achieved with HUJI 16 on the R2R manufacturing line were sufficient for application in an OLED device, it was decided to produce a S2S printed and sintered OLED device instead. As plastic foils are not compatible with the OLED production line available at Philips Lighting, ITO on glass needed to be used as the substrate. The spreading and sintering behaviour of HUJI 16 on ITO has been studied (cf. WP2 report), and with these optimised conditions, a shunt line pattern has been deposited on substrates provided by Philips. After photonic sintering in a S2S unit, the lines were covered with an isolating lacquer to prevent silver migration and sent to Philips for further device fabrication (Figure 22).

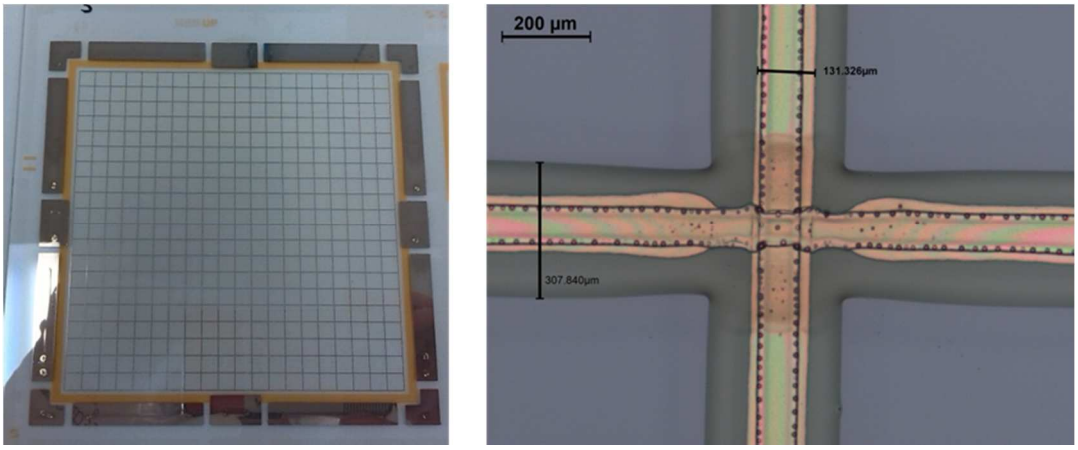

Figure 22: Photograph (left) and optical micrograph of a detail (right) of the semi-finished OLED demonstrator device after manufacturing at Holst Centre

Philips prepared samples of an OLED demonstrator. The OLED display is proven to work with the silver nano particle ink, but a lot of spray and satellites were observed from the nanoparticle silver ink (Figure 23). This spray is clearly visible, and it is obvious that it extends into the active area of the OLED. This reduces the lifetime of the OLED demonstrators. Also in the active area, small, uncovered droplets are found, as shown in Figure 24. As the shunt grid in the active area is covered by a protective resist that has a better adhesion than the silver, the demonstrator samples have been carefully cleaned before further processing.

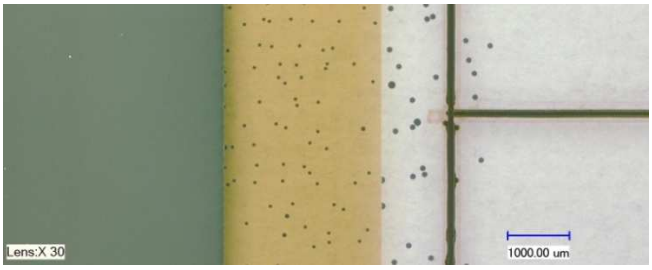

Figure 23 : Spray of silver ink near the bus bars of an OLED

Figure 24 : Small silver droplet in the active OLED area

In general, the OLED display is proven to work but removal of layers needs to be improved. With respect to adhesion and scratch resistance, the current silver ink HUJI16 requires scratch improvement, although predecessor HUJI nanoparticle inks had better scratch performance. Also spray can be circumvented by a better tuning, making silver deposition a viable option for OLED substrate manufacturing. It is expected that better sacrificial protection layers can be formulated.

Task 2: Thin film PV cell demonstrators (silicon and polymer)

ECN showed in WP5 that with selective laser structuring and inkjet of conductive ink material, a simple OPV cell structure can be made. In Figure 25, the bottom electrode, which has been generated by inkjet and laser structuring, is highlighted with a yellow line.

Figure 25: Close up of Organic PV cell. (Yellow lines = Bottom electrode)

Not the inkjet and laser technology and systems limit this size but the coating steps. Both technologies are software controlled and can be aligned with camera systems or physical means. This is seen effectively in Figure 26, where the inkjetted silver electrode has been placed on the lines in the OPV structures generated by laser ablation in the previous process steps. Based on these process steps, a large demonstrator was manufactured using the leaf OPV design on a 140 mm x 140 mm glass plate. This showed the flexibility of the processing with inkjetted nanoparticle ink materials.

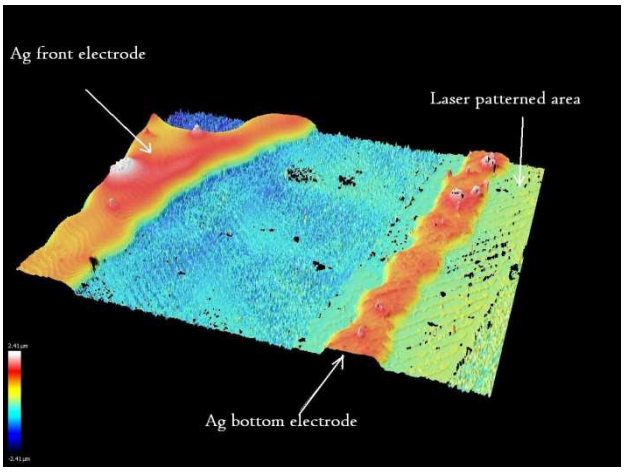

Figure 26: Optical scan of OPV leaf structure showing (a) silver ink bottom electrode and (b) laser structuring

HOLST used inkjet printing and photonic flash sintering of a commercially available conductive ink (Suntronic U5603) to prepare an organic solar cell demonstrator. The activities took part before LOTUS developed ink HUJI 16 had been available in the quantities required for these experiments. Both glass and PEN coated with a barrier layer have been used as substrates. The device architecture and a photograph are shown in Figure 27. After printing and S2S sintering of the silver inks, highly conductive PEDOT:PSS was inkjet printed on top, followed by spin coating of the photoactive layer. The devices were finished by evaporation of a counter electrode, and their current-voltage characteristics were measured. The photonically sintered devices (illumination time 5 s) were comparable in performance to devices thermally sintered for 6 hours (PCE 1.4 %), and no significant differences were found between flexible and glass substrates, as seen in Figure 27.

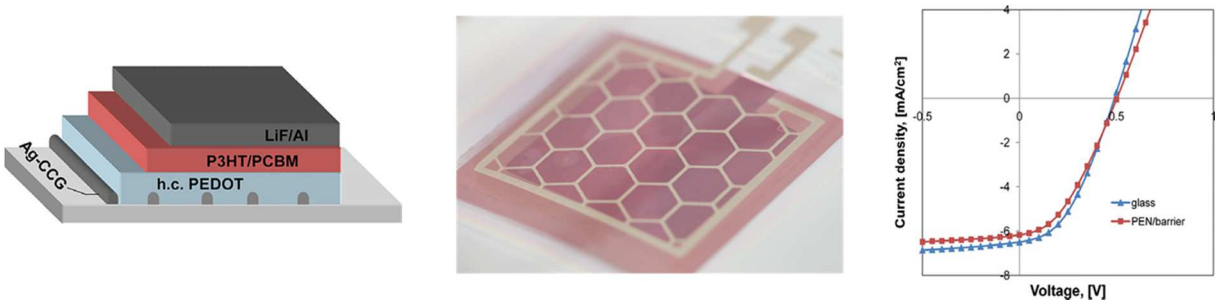

Figure 27: Device architecture (left) and photograph (centre) of OPV devices containing inkjet printed and photonically sintered silver current collective grids. Current-voltage characteristics of devices on glass and plastic foil (left).

ECN has demonstrated a CIGS backend module with an interconnection between cells generated using a silver conductive nanoparticle ink via an inkjet step. Isolation of the conductor from the cells was achieved using an acrylic inkjet ink. The connection via inkjet was made via (a) laser scribing to generate P2 scribe and then (b) inkjetting with the silver nanoparticle ink to connect to the right side top electrode (Figure 29).

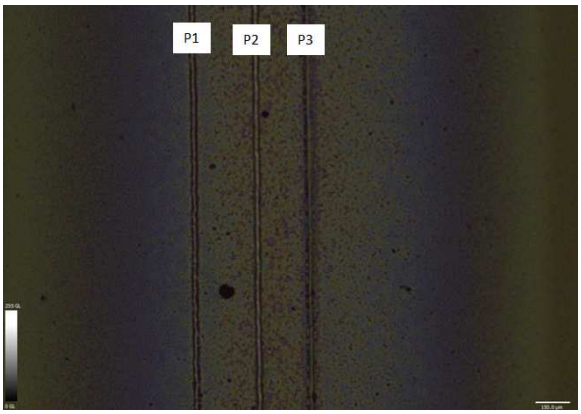

Figure 28: Isolation ink printed on P1 and P3 with P2 (middle) scribe lines prior to inkjet of silver nanoparticle ink.

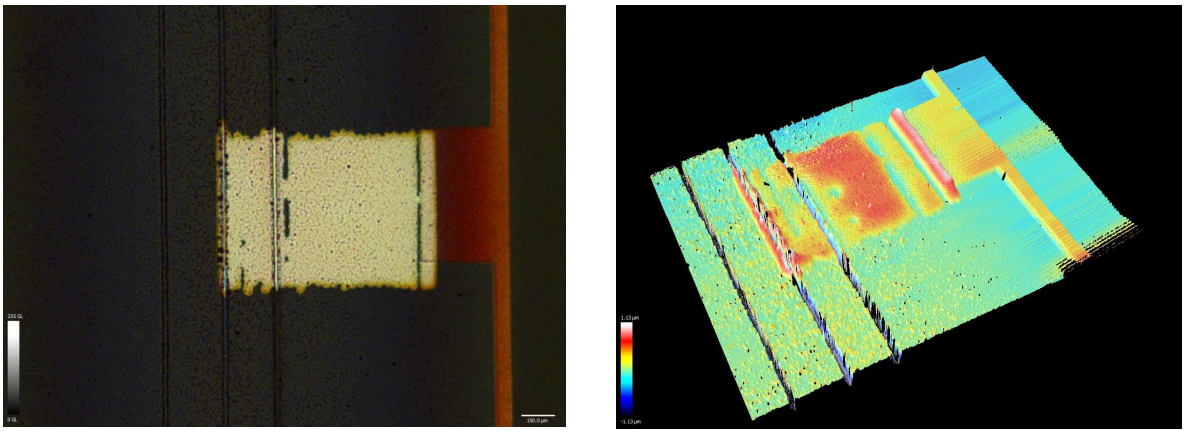

Figure 29: The left pictures shows the connection across P2 and P3 scribe lines using the inkjetted silver nanoparticle ink and on the right, the height of the inkjetted silver interconnection is shown (distance between outer scribes 500 micron).

Task 3: RFID demonstrator

In WP5, SMARTRAC designed the antenna to ensure that a functioning RFID transponder would be produced to work in the specific frequency range required by commercial readers.

This was possible after the optimisation of the printing and photonic sintering conditions for HUJI 16 by HOLST, as described in WP2, sections 1.1, 1.3 and 2. However, the redesign is also related to the dimension of the HOLST inkjet print head.

This new design represents a step forward from evaluation of current designs to specific designs, optimised for the achievable thicknesses and conductivities of the silver nanoparticle, photonically sintered inks. In addition, there was an optimisation of interconnect area for the RFID chip, to prevent shorting etc. related to the roll-to-roll processing of the HUJI16 ink on the HOLST tool.

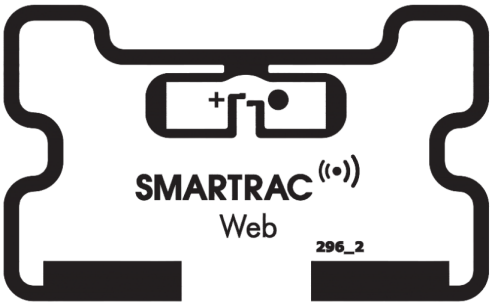

Figure 30: New SMARTRAC antenna design for inkjet printing of silver nanoparticle inks.

The final optimized design was then sent to HOLST for translation on the inkjet software. After optimisation of the R2R printing and sintering conditions, as described in WP2, sections 1.5 and 5, HOLST has produced several samples sets and roll material from R2R production of 20 – 30 metres length with the SMARTRAC antenna design using the HUJI16 ink and the XENNIA printer. The exact characterisation is described in WP2, section 5. The individual process steps are visualised in Figure 31.

Figure 31: R2R fabrication of RFID antennas. Inkjet printing (left), entering (centre) and exiting (right) of the photonic sintering unit.

High structural integrity has been maintained between design and the generated conductive trace from the nanoparticle ink. In addition, a high adhesion between substrate material and photonically sintered nanoparticle ink has been achieved.

Figure 32: Photonically sintered HUJI-16 nanoparticle ink antenna produced with the HOLST R2R tool.

The results for the RFID antennas with Monza4 RFID chips printed different substrate materials were extremely good. Briefly, the measured resistances of the antenna design inkjet printed with HUJI16 ink and photonically sintered with the HOLST tool are sufficiently low (5 – 10 mΩ/□/mil) to enable the antenna usage in the required application. Lower resistances can be achieved by 2 layer prints, but in R2R, this trend is accommodated by changes in DPI and in changes in the antenna width. R2R assembly of the chip on the antenna was achieved using commercial tools (Muehlbauer) using

a commercially available non-conductive paste adhesives (Figure 33). Measurement on Voyantic Tagformance lite measurement systems shows that the typical read range of the photonically sintered printed antenna with Monza4 RFID chip lies between 2-5 m, with the longer ranges being reached by lower resistance antennas. Results are comparable with an aluminium antenna, which has a thicker conductor trace (30 micron instead of 1 micron).

Chip on Antenna (top side) Chip on Antenna (top side) Chip on Antenna (underside)

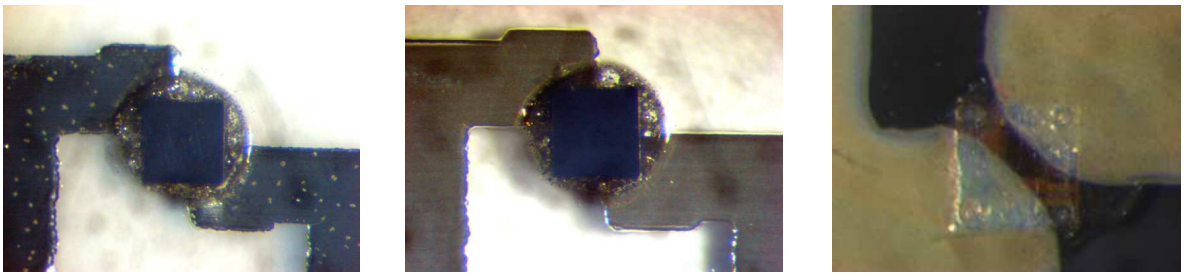

Figure 33: IMPINJ Monza4 chips assembled with adhesive on the photonically sintered nanoparticle ink antennas manufacutured with the R2R tool at HOLST.

Measurements First Samples Measurements R2R production samples

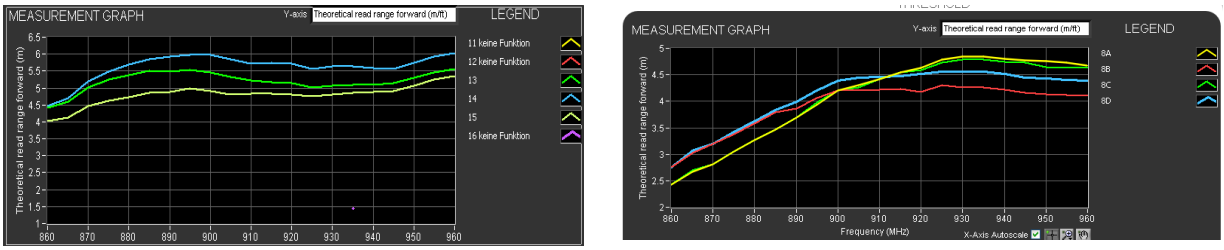

Figure 34: Voyantic Tagformance lite measurement of RFID transponder units after adhesive assembly of IMPINJ Monza4 chips on the photonically sintered nanoparticle ink antennas manufactured with the R2R tool at HOLST. Assembly with Muehlbauer assembly tools.

Main results of WP6

In work package 6 exploitation and dissemination of the LOTUS project results was dealt with.
This means that dissemination through presentations on conferences, seminars, workshops, summer schools etc. was performed. Special mention is for the master class *Printing Technologies for Electronics Applications* which was done in Berlin on the IDTechEx in April 2013 during which the range of printing and non-printing manufacturing and handling options for the new printed, organic and flexible electronics was assessed. This master class was performed by Holst Centre and ECN with contributions of FSU Jena and Hebrew University. In addition, Philips presented on the same IDTechEx Conference *The Value Chain of Inkjet Printing Conductive Inks*, in which the LOTUS project was shown.
More dissemination activities/results can be found in the *Plan for the use and dissemination of foreground* and in the list of main dissemination activities, list of publications, list of patents and list of exploitable foreground. This last list should be treated confidentially.