Optimizing the Performance of Metal Grid Conductors by Modifying Printing Conditions

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Abstract

Printed metal grid conductors can be used in thin, flexible and large area lighting sources based on e.g. light-emitting electrochemical cells (LEC). Similar to organic light emitting diodes (OLEDs), LECs are thin film electroluminescent devices, which can be processed from solution. However, LECs have a more simple architecture, and don't rely on air-sensitive charge-injection layers or metals for electron injection. This offers simplicity for manufacturing process, cost-efficiency and easier large scale manufacturing. Printing methods such as inkjet and flexography are suitable for manufacturing metal grid conductors needed in LEC devices.

The goal of this paper is to evaluate the potential of flexography and inkjet printing to manufacture metal grid conductors in industrial scale. Printing equipment that can be up-scaled to industrial scale is used and printing conditions are modified to meet the device requirements. Performance and properties of inkjet and flexographic printed conductors are compared. Finally, feasibility of the required industrial setup is evaluated.

Introduction

LEC technology

Typically LEC devices consist of one or two functional layers device that are sandwiched between two electrodes of which the emissive layer is ionic. When an external bias is applied the positive and negative ions of the emissive layer are displaced and an interfacial electric field is generated that allows for efficient hole and electron injection from air-stable metals.

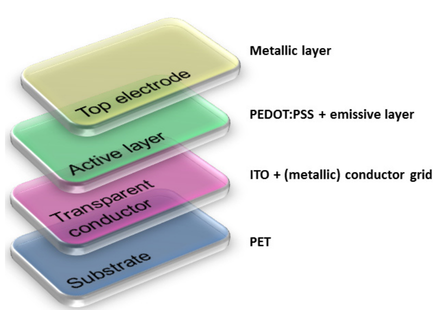

Figure 1. *Basic structure of a sandwiched LEC device.*

Two different LEC device architectures exist: sandwiched and interdigitated devices. In the latter the active layer is deposited on top of an interdigitated electrode structure. This paper focuses on sandwiched devices where the active layer is placed in between two large area electrodes (figure 1). At least one of the electrodes is transparent.

Objectives

In this work, the transparent bottom electrode of the LEC cell consists of ITO coated PET substrate (ITO-PET) with inkjet or flexographic printed metal grid conductors on top of it. These printing methods provide system flexibility for industrial setup, potential for high throughput and small details, and compatibility with different kinds of ink types. On top of the bottom electrode, PEDOT:PSS, emissive layer and top electrode are added by printing or coating methods. Basically, the whole LEC device could be printed, but this work focuses only on metal grid conductor printing. The metal grid conductor consists of 150 mm × 150 mm grid with 5 mm wide electrodes on all sides. Pedot coating is added afterwards.

The goal of the printing trials was to fabricate metal grid conductors namely honeycomb structures with as little surface roughness as possible, layer thickness of grid below 1 µm, layer thickness of electrodes in the range of 10-20 µm, grid line width 200 µm, good conductivity and good adhesion in processing conditions that simulate industrial production.

Materials and methods

Industrial-scale multi-nozzle inkjet printheads with 10 and 30 pl drop size and 128 nozzles (S-Class printheads from Fujifilm Dimatix) were used in combined single-pass and scanning mode where printheads are stationary and sheet substrate moves under the printheads. Because the native resolution of the printheads used is 50 dpi, several scans were required to increase the print resolution to 600 dpi. In industrial setup the same can be achieved with interlaced printheads. Printing speed of 150 mm/s was used.

Different commercial inkjet inks were tested in order to find the best ink for metal grid patterning. Ink testing was done with 30 pl drop size and after ink selection printings were done with 10 pl frop size. Two silver nanoparticle inks (Silverjet DGP 40LT-15C from Advanced Nano Products and NPS-JL from Harima) and one soluble silver cluster complex ink (TEC-IJ-060 from InkTec) were inkjet printed. Sintering was done in 140 $^{\circ}$C for 1 hour.

Preliminary flexographic printing trials for ink testing purposes were performed with a table top flexographic printer RK Flexiproof 100 from RK Print Coat Instruments. Different printing speeds were used to deposit the same honeycomb metal grid structure on the ITO-PET substrate via a flexible printing plate. The anilox roller was chromed and its cell volume was 13.6 cm^3/m^2. The effect of the sintering time on the printed layer quality was also looked at. R2R flexographic printing trials were performed with ROKO pilot printing machine. Honeycomb metal grids were printed onto the ITO-PET substrate. The cell volume of the chromed anilox roller was 9 cm^3/m^2.

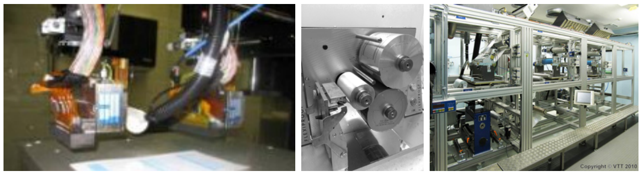

Figure 2. Inkjet and flexographic printers used in this study. From left inkjet printer with industrial scale printheads, table top flexographic printer and roll-to-roll flexographic printer.

Two different commercially available flexographic/gravure nanoparticle inks (PGi-722 from PChem Associates and TEC-PR-020 from InkTec) were printed with flexography at a speed of 10 m/min. The printed ink layers were dried in an oven. R2R printing trials were performed with InkTec TEC-PR-030 nanoparticle ink at a speed of 2 m/min. The samples were dried through the four ovens of the printer twice.

All inks are listed in table 1.

Table 1. Inkjet and flexographic inks and their properties.

Ink name	Printing method	Ink type	Particle size	Metal content
Silverjet DGP 40LT-15C	Inkjet	Silver nano-particle	40-50 nm	35 wt-%
NPS-JL	Inkjet	Silver nano-particle	5-12 nm	52-57 wt-%
TEC-IJ-060	Inkjet	Soluble silver cluster complex	-	12 wt-%
PGi-722	Flexography / gravure	Silver nano-particle	10-20 nm	50-65 wt-%
TEC-PR-020	Flexography / gravure	Silver nano-particle	20-50 nm	~30 wt-%
TEC-PR-030	Flexography	Silver nano-particle	20-50 nm	~50 wt-%

Commercial ITO (Indium Tin Oxide) coated PET (Poly Ethylene Terephthalate) substrate was used as substrate (OC50-ST504 from Solutia).

Print layout consisted of honeycomb grids, lines with varying line width and areas for contact resistance measurements.

Visual print quality, ink spreading, three-dimensional profile, ink layer thickness, surface roughness, square resistance, volume resistivity and contact resistance of both inkjet and flexographic printed samples were analyzed. The ink spreading was measured with Smartscope optical microscope. The layer profile and thickness were analyzed with Veeco Dektak 150 surface profilometer and layer roughness with Veeco Wyko white-light interferometer. The square resistance and volume resistivities were calculated from the measured line resistance, line dimensions, and layer thickness.

The contact resistivity between the silver patterning and the transparent ITO conductor was measured using lines printed at varying distance from each other. With this procedure, the line-to-line resistance can be reliably measured while eliminating any probe-to-line contact resistance terms. The probes were gently lowered onto the silver lines to ensure the silver layer remains unbroken. The transfer length method (TLM) was employed to extract the specific contact resistivity (ρ_C) and the ITO sheet resistance from the measurement data. Detailed information about this procedure can be found in [1].

Results

Ink and substrate compatibility

The biggest challenge in the printing trials was that the commercial ITO-PET substrate was found to have poor compatibility with both inkjet and flexographic inks resulting in excessive ink spreading and poor adhesion with some of the inks.

In inkjet printing with silver cluster complex ink there were lots of printability challenges resulting in satellites, missing nozzles and nozzle drying. Also after sintering there were pin holes in larger printed areas. Due to these problems this ink was abandoned from further trials. The two silver nanoparticle inks performed well during printing. However, NPS-JL ink had poor adhesion to substrate and also some nozzle drying was seen thus resulting in occasional missing nozzles. Due to this Silverjet DGP 40LT-15C ink was chosen for further trials.

To avoid excessive ink spreading in inkjet printing solvent evaporation was accelerated by using substrate heating up to the sintering temperature of 140 °C during printing. This resulted in fast ink curing because of immediate solvent evaporation without ink spreading and at the same time prevented also bulging and coffee ring effects not desired for conductors. The principle of heated substrate is presented in figure 3. More information on the effect of substrate temperature can be found in [2].

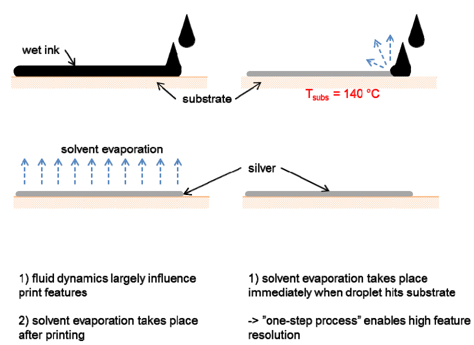

Figure 3. Principle of heated substrate and its effect on ink spreading.

Both flexographic inks had a good printability, but TEC-PR-020 ink had some adhesion problems and PGi-722 ink dried rather quickly onto the anilox roller, thus making the cleaning up extremely difficult. Plasma treatment (300 W, 5 min) of the substrates decreased ink spreading and allowed appropriate ink transfer. InkTec inks were chosen for further R2R experiments because of its better smoothness, cleanability and suitability to be used with common chromed anilox rollers. TEC-PR-030 flexographic ink was acquired for R2R experiments to ensure total compatibility of the ink with the flexographic printing process.

Roughness and print quality optimization

Challenge in inkjet printing was high surface roughness due to the fact that in inkjet printing features are made from separate small ink drops that might not set optimally to form an even ink layer [3]. In order to achieve low surface roughness heated substrate was used. Also optimization of print resolution resulted in low surface roughness and at the same time thin ink layer. Too high print resolution produced thicker ink layers than targeted and too much ink spreading. Also large ink areas behaved undesirable during sintering producing areas with uneven ink coverage. On the other hand too low print resolution resulted in ink layer which seemed to be made of separate dotted lines thus increasing standard deviation of surface roughness.

In flexography, ink was squeezed towards the edges of the printed features. This led to the formation of sharp edges that were separated from the actual printed layer and in which the layer thickness was larger than the average layer thickness. This squeezing is typical for flexography and cannot be eliminated totally. Figure 4 shows microscopic images of lines printed with inkjet and flexography.

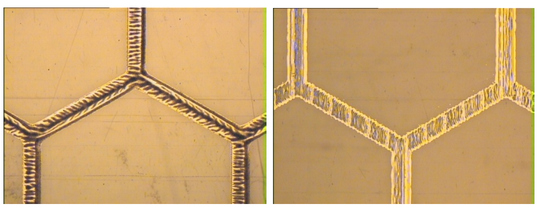

Figure 4. Microscope images of lines printed with (from left) flexography and inkjet with optimized printing settings (600 dpi, 140 °C substrate temperature).

Target line width was 200 µm, but because of ink spreading actual line width was at least 300 µm (Figure 5). In addition 400 µm and 600 µm lines were tested and also they spread correspondingly. Horizontal lines spread a bit more than vertical lines. Since in inkjet printing there is no contact pressure present in printing inkjet lines spread less than corresponding flexographic lines. Line width could be decreased to desired level by using thinner lines than target line width in the print layout thus compensating ink spreading.

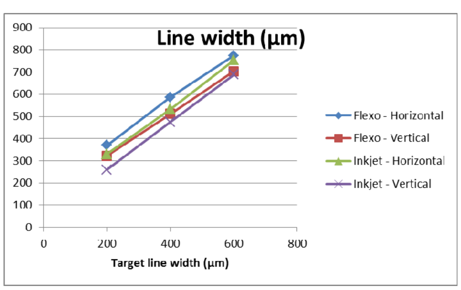

Figure 5. Line width of inkjet and flexography printed horizontal and vertical lines when target line widths were 200, 400 and 600 µm.

Target layer thickness for grids was below 1 µm. Both flexography and inkjet printed lines were able to meet this goal (figure 6). Inkjet printed grid lines were a bit thicker, but had higher standard deviation due to striping caused by adjacent nozzles. Target layer thickness for electrodes was 10 µm, but with three inkjet printed ink layers only 1.5 µm layer thickness was achieved thus indicating than at least 10 ink layers would be needed. However, different ink layers were placed nicely on top of each other without affecting the line width compared to one ink layer.

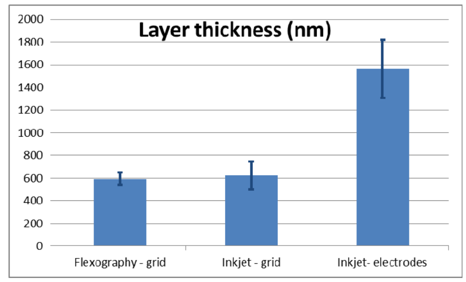

Figure 6. Layer thickness for inkjet printed grids and electrodes and for flexography printed grids.

Surface roughness was higher with flexography than with inkjet, but inkjet had higher variation (figure 7). Inkjet ink particle size was 40-50 nm and with smaller measurement area the R_a value is in the same range thus indicating that there is no room for roughness improvement since particle size has already been reached. In flexography, there were lots of unsintered particles present in the printed layer, thus making also the small-scale roughness high.

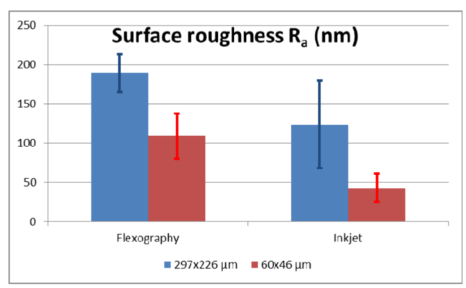

Figure 7. Surface roughness and its variation for inkjet and flexography printed grids.

Electrical performance

Electrical performance was found good with both inkjet and flexographic printed grids (Figure 8). Volume resistivity values were in the order of 0.01-0.02 mΩ cm. Flexographic grids had better conductance than inkjet, probably due to higher metal loading. Un-sintered nanoparticles, printing process related stripes and waviness, poor ink layer leveling, and adhesion issues can also decrease the conductance. Corresponding square resistance values were in the order of 400 mΩ/square. Inkjet printed layers had higher resistance variations probably due to striping and waving.

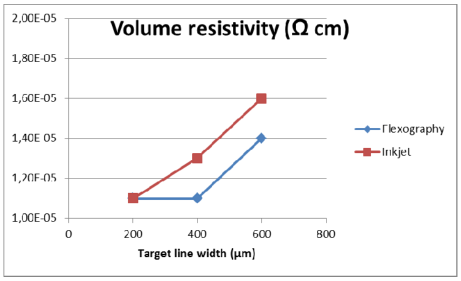

Figure 8. *Volume resistivity of inkjet and flexography printed lines.*

Specific contact resistance were in the range of 0.5-15 mΩcm^2. Increasing the sintering time can decrease not only the resistivity of the printed grid lines, but also the specific contact resistance between the silver lines and the underlying ITO layer.

Conclusions

As a conclusion, both inkjet and flexographic printing were found suitable for fabricating metal grid conductors since surface roughness, layer thickness and electrical performance met the target values when printing conditions were carefully optimized. Some compromises had to be made between adhesion, surface roughness, layer thickness and process reliability requirements. However, further testing is needed to investigate if these grids can be used in LEC devices since surface roughness of the grid might cause shorts in the LEC devices after all. Also adhesion of the girds should be studied further since it is also a critical property in LEC devices.

Inkjet printing is especially suitable when customization of the printing pattern, fine details, integration with existing production lines and multi-layer printing is required. Flexography in turn is ideal when higher throughput or more reliability is needed. Since results presented in this paper were made with printing equipment suitable also for industrial production, these results should be up-scalable for production environments.

References

[1] Mark Allen, Elina Jansson, Liisa Hakola, Sanna Rousu, Riikka Suhonen, Ari Alastalo, Printed conductor grids on transparent electrodes, Proceedings of LOPE-C conference, Munich, Germany (19.-21.6.2012), 6 pages.

[2] Liisa Hakola, Metal grid conductors for LECs by using high-speed inkjet printing, SID2012 Spring Meeting, Stockholm, Sweden (7.-8.5.2012).

[3] Liisa Hakola, Improving quality of inkjet printed metal nanoparticle conductors, Proceedings of IS&T NIP 22 conference, Denver, USA (2006), pages 99-102.

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Author Biography

Liisa Hakola graduated as Master of Science for Graphic Arts from Helsinki University of Technology in 2002. Since her graduation Liisa has worked at VTT as Senior Scientist in the field of printed functional solutions. Her research work focuses on industrial inkjet printing, new coding methods as well as printed electronics and diagnostics. She has published several international scientific papers as well as given conference presentations.