Manufacturing of polymer light-emitting device structures

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ABSTRACT

The gravure printing technique is currently under investigation as a possible method for the roll-to-roll production of OLEDs in the 6th framework EU funded project entitled ROLLED - "Roll-to-roll manufacturing technology for flexible OLED devices and arbitrary size and shape displays". The objective in the project is to fabricate an entire OLED structure by using roll-to-roll manufacturing methods and to examine, how the commercial production could be set up and integrated into an existing printing process. In order to attain a roll-to-roll compatibility, all the materials, inks and device structures need to be suitable for printing. Since, such OLED device structures are very sensitive to moisture and oxygen, high barrier materials to be applied as wet chemical coatings on transparent polymer films such as PET by common roll-to-roll coating techniques have been investigated. The barrier films on their respective substrates act as front and back side encapsulation materials, where the front side encapsulation material is to be used as a transparent and flexible substrate for OLED fabrication. The transmission rates to be achieved for both front and back side encapsulation for oxygen and water vapour are 5 mg m⁻²day⁻¹ (corresponding to 7 cm³ m⁻²day⁻¹ for O₂). In this paper, we show how light-emitting devices manufactured by gravure printing operate compared to the ones manufactured by traditional methods. Furthermore, we present recent results on the development of ITO nanoparticle coatings, cathode inks and flexible barrier materials.

Keywords: Gravure printing, polymer light-emitting devices, roll-to-roll, ITO, flexible barriers

1. INTRODUCTION

Polymer electronics has grown into a promising candidate to replace some silicon applications. Conjugated polymer materials are very attractive to be used as a part of simple device structures such as electroluminescent displays and polymer solar cells.¹ In generally, the fabrication is carried out in traditional and expensive batch processes like vacuum evaporation technique.² However, a new interesting way is to apply roll-to-roll printing methods for the manufacturing of the flexible devices.³ This would decrease considerably the fabrication costs.

2. FLEXIBLE BARRIER MATERIALS

The purpose of encapsulating is to protect devices from adverse environmental conditions such as moisture, mobile-ion contaminants, but also temperature changes, radiation, and mechanical and physical damage in order to increase their long-term reliability. The lifetime of an encapsulated polymer light-emitting device (PLED) is significantly increased compared to an unencapsulated device. In the application of PLEDs to practical displays, there are many fundamental issues to be considered and the device stability is one of the most critical issue from a practical point of view. The operational lifetime should be between 100 h and 10'000 hours, depending on the application. For example, a simple encapsulation technique to protect the device is to apply a thin epoxy adhesive layer between the device and encapsulant glass.
The specification for barrier properties in this project is based on the present knowledge of the PLED technology. One difficulty for definition of this requirement is the measuring accuracy of the permeability. Typically used MOCON Permatran quantitative metrology equipment is limited to the accuracy of $5 \times 10^{-3}$ g m$^{-2}$ day$^{-1}$. However, based on the present knowledge permeability of this value of $5 \times 10^{-3}$ g m$^{-2}$ day$^{-1}$ should still be adequate for lifetimes pursued in the project.

2.1. Front side encapsulation

The front side encapsulation material acts as a substrate for the application of the transparent oxide anode which is part of the completed PLED structure. Its purpose is to protect the device against in-diffusion of water vapour and oxygen from the front side. Therefore, it must have excellent barrier properties. A target value of less than $0.005$ g m$^{-2}$ day$^{-1}$ was specified in the working programme for the transmission rates of both water vapour and oxygen. In addition, the front side encapsulation has to be flexible in order to preserve the flexibility of the whole device and has to supply a smooth surface to meet the requirements of the thin coatings of the PLED structure. Additionally, it needs to be transparent, since the light from the PLED will be emitted through the front side.

Since the state of the art transparent flexible substrates prepared by PVD or CVD techniques are still prepared by expensive batch processes, a novel concept based entirely on roll to roll wet coating processes is being developed. As in standard high performance barrier coatings, a multilayer approach is being used, combining glassy inorganic layers for a high barrier functionality and polymer-like layers for defect isolation, mechanical support and protection. Details of that approach will be presented elsewhere. The current performance of barrier substrates (water vapor transmission rates between $10^{-2}$ and $10^{-1}$ g m$^{-2}$ day$^{-1}$) is still limited by defects, but bears considerable potential for improvements.

2.2. Back side encapsulation

The back side encapsulation is supposed to be applied to the completed OLED in a final coating or lamination step. Its purpose is to protect the device against in-diffusion of water vapour and oxygen from the back side. Therefore, it must have excellent barrier properties. A target value of less than $0.005$ g m$^{-2}$ day$^{-1}$ was specified in the working programme for the transmission rates of both water vapour and oxygen. In addition, the backside encapsulation has to be flexible in order to preserve the flexibility of the whole device. It does not, however, need to be transparent, since the light from the OLED will be emitted through the front side.

Since transparency is not required, it is possible to use metal foil in order to achieve excellent barrier properties, aluminium foil being the most cost effective example. For easier handling and in order to prevent electrical shorts, the aluminium foil is laminated to a suitable polyester foil as a support as shown in Figure 1. This stack can then be laminated to the OLED device. For both lamination steps, a suitable adhesive is necessary.

![Figure 1. Lab scale back side barrier stack prepared without OLED structure.](image)

<table>
<thead>
<tr>
<th>epoxy thickness µm</th>
<th>WVTR g m$^{-2}$ day$^{-1}$</th>
<th>OTR cm$^3$ m$^{-2}$ day$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.006</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>10</td>
<td>0.009</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>
Laminates were produced on the pilot coating machine using various configurations and adhesives. In first trials, the aluminum foil was used as the main web and coated with the adhesive, whereas the PET foil was laminated against this coated web. Later, the roles were reversed in order to have a shorter web path for the aluminium foil. The laminates were then cured at room temperature on the roll. In summary in Table 1, water vapour transmission rates below 0.01 gm⁻²day⁻¹ were measured on a MOCON Permatran instrument. Also oxygen transmission rates were below the detection limit of the MOCON OxTran instrument, which is around 10⁻⁵ gm⁻²day⁻¹.

3. POLYMER LIGHT-EMITTING DEVICES

Gravure printing offers a fast and cost-efficient roll-to-roll technique with high potentials in the manufacturing of polymer light emitting devices and adequate patterning resolution. In this technique, the pattern to be printed is engraved into a rotational printing cylinder. During printing, the printing ink is filled into the engraved cells by the use of a flexible doctor blade to remove the excess ink and to ensure that the cells are filled with a reproducible amount of ink and is then transferred to the foil when the cylinder is brought into contact with the surface of the substrate foil. However, extremely thin and uniform PLED structures are setting high demands on the process.

3.1. Printing of patterned ITO anodes

The aim was the development of a patterned anode of transparent conducting ITO on PET foils by a printing process based on ITO nanoparticle dispersions. The ITO patterns thus prepared were to be used as transparent anodes in PLED devices structures. Before the start of this project, crystalline ITO nanoparticles had been developed and dispersed in different solvents mainly for large area coating (e.g. by spin coating). By addition of a small amount of a polymerizable hydrolyzed silane and a photostarter, transparent conducting ITO coatings were thus obtained on plastic substrates including foils by a UV-curing at low temperatures (<130°C) with a sheet resistance of 2 to 5 kΩsq and a transmittance of 90 % in the visible range (thickness 500 nm). A post treatment under reducing conditions (N₂/H₂) at low temperatures (<130°C) resulted in a further decrease in the sheet resistance below 1 kΩsq.

![Figure 2. Photographs of a) the lab-scale gravure printing machine, b) the gravure plate with different patterns (areas are 37x127 mm² in size), and c) the diamond-engraved cells pattern (110 lines/cm).](image)

In a first set of experiments it was intended to obtain full-tone printed areas with a high thickness homogeneity using a lab-scale gravure printer for testing (Figure 2a, Labratester - N. Schläfli Maschinen) and a plate with rectangular stripes (Figure 2b & 2c, 37x127 mm² each) in order to find the working parameters for ITO coatings such as the feasible printing speed or the characteristics of the gravure cavities. In general, film formation in gravure printing requires a coalescence of adjacent, single liquid dots while at the same time, however, a spreading of the liquid droplets or of the film beyond this coalescence has to be avoided to retain the printed structures. This requires an elaborate adjustment of the rheological properties of the printing inks and a thorough control of film drying.

Typical printing speeds up to 40 m/min thus could be realized without loss of homogeneity. While homogeneous coatings could be generally obtained for line densities ranging from 40 to 210 lines/cm, this parameter also fundamentally determines the thickness of the resulting coatings as the volume of the engraved cavities is decreasing with the line density. In view of the final application to a direct patterning, however, this means that a compromise has to
be found between the desired coating thickness and the required resolution of the printing as the rheology of the inks can only be varied in certain limits mainly given by the limitation in the solid content and by problems arising from the use of printing additives. Depending on the ITO solid content in the inks and the geometry of the gravure cells, thus thicknesses ranging from 0.2 to more than 1 µm were realized in a single printing step.

Different ITO inks based on solvents with medium and high boiling points were tested. In addition, comparative experiments with different surface modifiers for ITO were initiated to minimize the interaction between the particles during film formation as a major requirement for optically transparent coatings. The total content of solvents and additives in the printing ink generally is a very important parameter for coating quality, as it also influences the film drying and determines the content of organic residues in the resulting ITO film and hence the porosity.

![Graph showing transmission spectra](image)

**Figure 3.** Typical transmission spectrum of gravure printed ITO coating on PET foil (Melinex ST505, 100 µm).

Optically flawless coatings were obtained using ITO nanoparticle concentrations of 40 wt% or higher with typical thickness between 300 and 900 nm. The corresponding sheet resistance of the coatings is on the order of 2 to 10 kΩsq after UV curing. The typical optical transmission spectra of such coatings measured by a Cary 5E spectrometer with air as reference (Figure 3), shows a high transmission in the visible part and the typical plasma absorption in the NIR. An optical haze of well below 1 % was obtained which is comparable to that of the PET substrate. The corresponding SEM (scanning electron microscope) surface image of such an ITO coating (Figure 4) shows a homogeneous distribution of ITO nanoparticles as obtained by controlling the film drying. Based on these results, also electrode patterns were printed with line widths on the order of 100 µm and high optical transparency.

![SEM image](image)

**Figure 4.** SEM image of a homogeneous and clear gravure printed ITO coating on PET film.
These initial printing experiments showed no significant change in the coating properties compared to those obtained by the spin-coating technique and the realizable thickness range is similar, however, the ink composition is very different. While the sheet resistance is on the same order of magnitude, the optical transmission appears to be a more critical issue probably as the drying time of the wet film is extended and thus gives more time for an influencing by the atmosphere. On the other hand, the longer drying stage also offers new possibilities for a better control of film formation by a post-deposition treatment. A controlled organization of the particles into a denser film not only guarantees a good contacting and higher conductivity but is also important to govern the optical properties.

3.2. Printing of the hole injection layer, PEDOT:PSS

A thin layer of the intrinsically conductive polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene doped with poly(styrenesulfonate)) is essential in PLED structures for several reasons, when ITO is used as an anode layer. Firstly, to smooth the surface of the ITO layer and, secondly, to increase the work function of an anode from 4.9 eV to 5.2 eV, which enhances the injection of holes into hole transport or emitting layers. Normally for an efficient device performance a 50-100 nm thick PEDOT:PSS film is deposited on ITO. PEDOT:PSS is usually deposited by spin coating from an aqueous solution resulting in a planar and uniform film (R$_{\text{rms}}$ < 4 nm). In this work, PEDOT:PSS (Baytron®P VP CH8000) was gravure printed successfully with a IGT printability tester. Extremely thin and uniform structures will set high demands for the process but the suitability of gravure printing in the fabrication of extremely thin and uniform films was demonstrated.

An aqueous dispersion of PEDOT:PSS has been used in order to planarize the ITO surface (sputtered ITO on PET). The gravure printed PEDOT:PSS caused inhomogeneous films on the surface of the anode, even when the surface of indium tin oxide (ITO) anode was oxygen plasma etched. The main reason for the non-uniformity is the poor wetting of aqueous PEDOT:PSS on the surface of the hydrophobic ITO. Therefore, it was necessary to modify the standard PEDOT:PSS in order to improve the surface quality of the film.

Figure 5. Modified PEDOT:PSS films gravure printed by using different cell sizes (depth of the pyramidal cell from 35 to 45 µm).

Much better wetting properties were achieved by adding a surfactant and a wetting agents to the standard PEDOT:PSS formulation. Compared to the films that were spin coated with standard PEDOT:PSS, the uniformity of the gravure printed films were in the same range as in spin coated films when using a mesh with 70 lines/cm and cell depths between 35 to 45 µm (Figure 5), corresponding to cell volumes between 6.4 ml/m$^2$ and 11.4 ml/m$^2$. 
Furthermore, the effect of additives on the PLED performance was investigated. The spin-coated devices based on modified PEDOT:PSS ink showed no significant differences in brightness and current density compared to the devices made from the unmodified PEDOT:PSS (Figure 6).

Table 2. Average film thickness of the modified PEDOT:PSS and the standard deviation (SD) at five different points of the same film.

<table>
<thead>
<tr>
<th>cell depth</th>
<th>45 µm</th>
<th>40 µm</th>
<th>35 µm</th>
<th>30 µm</th>
</tr>
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<tbody>
<tr>
<td>Thickness (nm)</td>
<td>78</td>
<td>53</td>
<td>44</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>51</td>
<td>41</td>
<td>23</td>
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<td></td>
<td>86</td>
<td>54</td>
<td>43</td>
<td>23</td>
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<td></td>
<td>85</td>
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<td>43</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>55</td>
<td>42</td>
<td>26</td>
</tr>
</tbody>
</table>

| average (nm) | 84    | 53    | 43    | 23    |
| SD (nm)      | 3.4   | 1.8   | 1.1   | 1.8   |

Figure 7. 2D profile of a 60 nm thick modified PEDOT:PSS film, where the film was gravure printed with 70 lines/cm mesh and 40 µm cell depth. The inset shows the printed pattern and profile line (in white).
The thickness and resolution of the printed films was characterized using white light interferometry. The adequate thickness values were sufficient when the depth of the cell was either 40 or 45 µm as demonstrated in Table 2. Furthermore, the measured thickness values showed good uniformity of the film in all cases. In addition, the resolution of the imprint was improved significantly, as shown in the 2D profile in Figure 7, where the edge defect of below 400 µm was sufficient.

### 3.3. Printed PEDOT:PSS/PFO double layer structure for PLED

A polyfluorene emitter (PFO, blue emitting polymer) was used to examine printability on the hole injection PEDOT:PSS. First the modified PEDOT:PSS ink was gravure printed with a speed of 60 m/min and a cylinder pressure of 500 N on the cleaned and oxygen plasma etched commercial ITO-PET (Rsq of 50 Ωsq) substrate. The thickness of the PEDOT:PSS was 53±2 nm. 4.5 mg/ml PFO ink in chloroform/anisole solvent mixture with the volume ratio of 1:1 was gravure printed using a cell depth of 60 µm. The corresponding calcium injection layer and silver cathode were vacuum evaporated at the base pressure of 10^-6 mbar. The active area was 16 mm². The luminance-current density-voltage (L-I-V) and efficiency measurements were carried out at ambient conditions without encapsulation of the device.

![Graphs](image-url)

Figure 8. Characteristics of a partially printed PLED; a) luminance vs. voltage, b) current density vs. voltage, c) external quantum efficiency vs. voltage, and d) normalized electroluminescence of PFO.
The *L-I-V* characteristics of the printed PFO devices are shown in Figure 8a-c. The gravure printing of both polymers layers was successfully done resulting in a good performance of the device. The turn-on voltage for light emission at 1 cd/m², and the brightness of 100 cd/m² were observed at 3.7 V and 5.0 V, respectively. Higher current densities indicate non-uniformity of the PFO layer after printing. A maximum external quantum efficiency of 0.1 % was achieved at the bias voltage of 6 V. For reference, the electroluminescence spectrum of the PFO polymer is shown in Figure 8d.

### 3.4. Cathode ink development

Though printable conductive silver inks are commercially available, they cannot be used readily as cathodes as silver has an unsuitable work function for efficient device performance. On the other hand, metals with low work function (e.g. Ca, Ba, Li, Na, Mg, Al) tend to oxidize easily and the oxidized metal surface prevents the ohmic contact between the metal particles thus reducing the conductivity. Also these metals are reactive towards many materials, which limits the choice of solvents, binder materials and additives.

But there are some additional important aspects in the development of the cathode ink. A good contact between organic layer and cathode is crucial. Therefore, the solvent has to be chosen that it does not dissolve the underlying layer. Also the curing temperature of the cathode ink has to be lower than the glass transition temperature of the organic material and the substrate. The oxidation of the cathode material can, for example, be prevented by protecting the metal surface with molecules. In the case of aluminum the intrinsic oxide layer can also act as a protective layer and prevent further oxidation. However, preparation of the ink and printing have to be done in inert atmosphere. In this study, Al and Mg were selected as cathode material for the cathode ink preparation. Commercial metal powders of 325 mesh (< 44µm) do not conduct due to the oxide layers on the metal particles, but ball milling of Al and Mg in hexane yielded around 5 µm particle size and a conductive metal powder. Besides the particle size, the shape of the particles can be modified. After milling, hexane was removed.

All manipulations were done in Ar or N₂ atmosphere, and solvents were dried and distilled before use. Printing tests were done on 36µm thick PET-film in a glove box with an IGT table top printability tester with a raster patterned printing cylinder. The electrical resistance, *R*, was measured using a multimeter with two contact pads, which were placed one centimeter distance apart. THF and toluene were used as solvents and polystyrene and PMMA as binders. The lowest resistances of 1 Ω for the Al ink and 5 Ω for the Mg ink were achieved with a toluene/polystyrene based ink.

![Figure 9](image.png)

Figure 9. Photographs of a gravure printed aluminum ink; a) raster 40 µm, particle size 5 µm, dispersant amount 2 wt%, *R*=1.5 kΩ, and b) raster 40 µm, particle size 1 µm, dispersant amount 5 wt%, *R*=3 MΩ.

A closer look at the imprints showed poorer printing quality due to improper wetting of the ink, as seen in Figure 9a. Also sedimentation of the metal particles from the ink matrix was a problem. By using surfactants the printability of the ink can be improved (Figure 9b). However, at the same time the conductivity of the ink suffered: the resistance of the gravure printed sample increased from 1.5 kΩ to 3 MΩ. More work has to be done to find proper surfactants and their concentrations in the ink. As a promising result, further optimization of aluminum ink and printing parameters resulted in uniform films as shown in Figure 10.
4. CONCLUSIONS

In conclusion, polymer LEDs based on gravure printed hole injection and light-emitting polymer films were fabricated successfully. The printed thin films achieved good uniformity over a large area showing the feasibility of a roll-to-roll manufacturing of polymer thin film based flexible polymer LEDs. Furthermore, we have presented recent results on the development of ITO nanoparticle coatings, cathode inks and flexible barrier materials.

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