Polymer Light Emitting Diodes Made by Inkjet Printing

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Abstract

Since its discovery in 1989 (1,2), electroluminescence from conjugated polymers has been a field of intensive research. One particular advantage of polymers compared to their small molecule counterparts is their processability from solution. This makes them the ideal active layer to be used for flat panel displays because the different colors can be inkjetted (3) economically even onto relatively large substrates. Inkjet technology for polymer light emitting diodes (PLEDs) and full color displays, however, is not fully developed yet, and a detailed understanding of the underlying principles and the interaction of printhead, ink and substrate has not been achieved thus far. This paper presents performance data of inkjetted PLEDs and compares them with the respective spin-coated devices. The results show the importance of the film homogeneities of the functional layers and how they can be influenced by various jetting parameters. Cross sections of inkjetted drops are vastly different depending on the drying conditions (underlayer, substrate temperature, formulation, surrounding atmosphere). Devices have been prepared on a substrate with a simple, low resolution photoresist structure. These devices show that the PL-image alone is not sufficient to predict the resulting EL image.

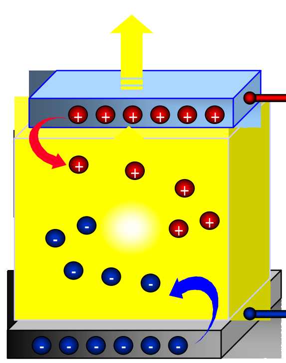

Figure 1, Simplified device configuration and principle of a PLED made of a typcial conjugated polymer, PPV

Introduction

Organic light emitting diodes based on conjugated polymers have traditionally been made by spin-coating. A simplified structure of such a device is depicted in Figure 1. A substrate (usually glass) coated with a transparent anode (usually ITO, Indium Tin Oxide) is precoated with an intermediate hole injection layer (PANI or PEDOT) and then with the active layer, 70 to 120 nm of a conjugated polymer. An electron injecting cathode containing Ca, Ba, Al or other injecting metals is evaporated on top of the film. After encapsulation and contacting, electroluminescence can be measured through the glass in dependence of applied voltage and current. Typical performance data for a spin-coated device of SuperYellow (PDY 132 from Covion Organic Semiconductors) are summarized in Fig. 2.

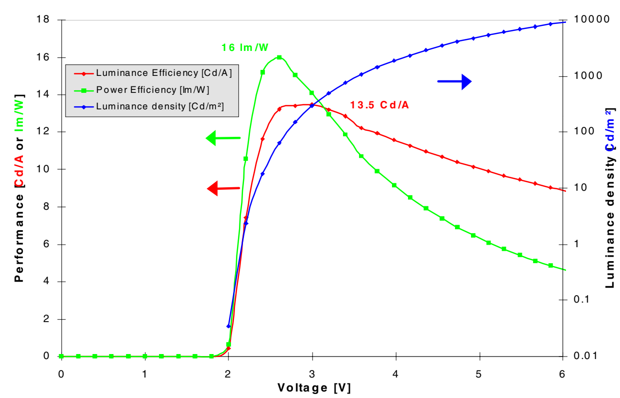

Figure 2. Typical performance values of spin coated SY.

Recent advances in the development of conjugated polymers for PLEDs have resulted in the availability of the basic colors Red, Green and Blue (4), however full color displays are not accessible by spin-coating. Inkjetting as a high resolution, non-contact printing technology that can easily handle pre-structured rigid substrates offered itself as an alternative deposition method. For a number of reasons, piezoelectric drop-on-demand printing is the method of choice (4), but since every printed dot has to fulfil its optoelectronic function as a spatially confined PLED device, simply delivering the RGB polymer solutions into the right spots is not sufficient to obtain a functional, defect-free, long-lifetime flat panel display (FPD). Aside from the traditional inkjet issues such as stable firing, drop directionality, head / ink compatibility, and nozzle-plate wetting, the development of inkjet as a display production technology therefore also requires to address the interaction of the drops with the pre-coated substrate after impact, drying and the resulting film morphology, homogeneity of the film thickness, and the formation and function of all interfaces. In order to get a better understanding of the parameters that influence the performance of an inkjetted compared to a spin-coated device, simple model experiments were carried out using either an unstructured pre-coated substrate or a simple test device structure with low resolution photoresist pixels. The results show how changing the drying conditions influences film formation and how crucial it is to actually check the inkjetted device.

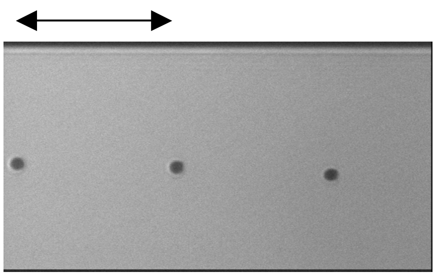

Figure 3. SY fired through a Xaar 360 (A Phase) at 500Hz and 28V. The arrow indicates the distance of 411µm between the A phases of the Xaar head.

Inkjetting of LEP Materials

All inkjet experiments where carried out using a Litrex 80L piezo micro deposition system with a Xaar 360 print head. The nozzle pitch of this head is 137µm. Because of the shared-wall design of this print head, only every 3rd nozzle ("A phase") was used for printing.

The already mentioned poly-phenylene vinylene (PPV) from Covion, PDY132 (commonly known as SuperYellow or SY), was used as the light emitting polymer (LEP). The ink-jettable solution had a concentration of ca. 1.4% of the polymer in an aromatic solvent. Table 1 summarizes the physical properties of this LEP formulation.

Stable firing conditions were obtained at 500Hz with a head voltage of 28V. The formulation formed drops with short straight ligaments that caught up with the main drop after approximately 400µm, as can be seen in Figure 3. Since the distance between head and substrate was ca. 500 µm, these ligaments had no influence on drop placement accuracy. The drop volume at these print conditions was approximately 40pl with a corresponding in flight drop diameter of 42µm. The average drop velocity was 4.5 m/s. Although the ink fired well, there were variations in drop velocity, drop volume and drop directionality between the nozzles of the print head. The angle deviations between all nozzles of the used print head are shown in figure 4. This is due to this particular print head and needs to be improved for the printing of high resolution full color displays where misplacement of drops is very critical. Suitable heads for this application are currently being developed (5). However, for the printing of monochrome test devices, the head performance is sufficient.

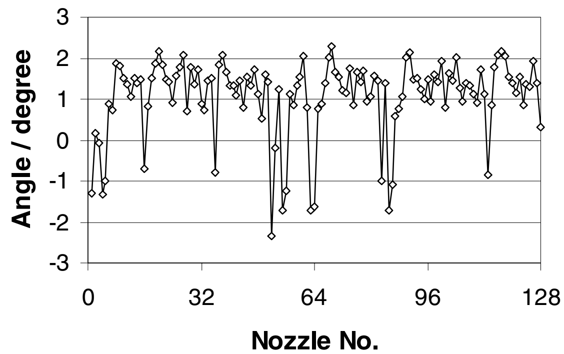

Figure 4. Relative angle deviations in respect to 90°.

Table 1 Physical properties of the used SY formulation.

Polymer concentration (g/l)	13.81
Surface tension (dyne/cm)	32.5
Viscosity (mPas)	13.03
Contact angle wet SY on dried SY (degrees)	60
Contact angle SY on PEDOT and ITO (degrees)	<10

Drying Behavior of LEP Drops

As has already been pointed out, finding printing conditions that allow an active device to be formed is the most important difference between conventional inkjet printing on paper and printing of LEPs. Ideally, a flat and homogeneous film with a film thickness of 70 to 120 nm would be formed on the PANI or PEDOT surface. It is therefore useful to look at the drying behavior of LEP drops as a function of substrate temperature on unstructured substrates. The drops were printed onto glass substrates fully covered with ITO and onto substrates with an additional 20nm PEDOT layer. The substrate temperature was varied by heating the chuck that keeps the substrates at their aligned position. The height profiles of the dry drops were measured with a Dektak3ST profilometer, the results are are shown in Figure 5.

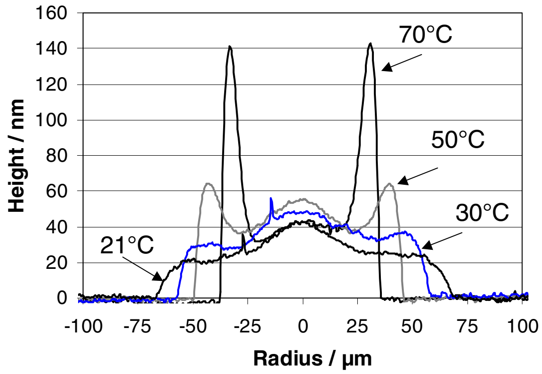

Figure 5: Profilometer scans through ink jetted drops of SY that were printed onto PEDOT coated substrates at different temperatures.

There are two effects that are noteworthy. First, the width of the drop decreases with increasing temperature. And second, the profile of the drops changes form a dome-like shape to a pronounced "coffee stain" shape with increasing temperature. The decrease in width is due to self pinning of the LEP ink on the substrate. This pinning is a result of the wetting properties of the ink. The wet LEP ink does not wet the dry LEP film as well as the PEDOT surface. At increased temperatures, the rim of the drop dries quicklier and creates an unfavored underlying polymer layer that stops the spreading, resulting in a smaller drop diameter.

It is interesting to note that the contact angle of a SY solution on dried SY films is 60 degrees. Practically this means, that the ink jetted pixels should be filled in one run, or that an ink with a high boiling point solvent must be used to prevent the film from drying while printing is still underway. For the test substrates we followed the first approach.

The SY formulations wet PEDOT very well with contact angles below 10 degrees. When considering the film homogeneity on a flat unstructured surface, improved wetting results in improved film homogeneity which will also improve the film homogeneity in a confined pixel. The exact measurement of the contact angles of the LEP formulations on ITO and PEDOT is difficult. However, the formulations tend to wet ITO better than PEDOT, as can be seen from the drop diameters of dried drops on ITO in comparison to those on PEDOT (Figure 6).

Figure 6 shows the diameter of dried drops on ITO and PEDOT as a function of temperature. The drop diameter for this formulation is always slightly bigger on ITO than on PEDOT proving that the wetting of ITO is better than that of PEDOT. Not only for film homogeneity, but also for the formation of a good electrical contact is a better wetting of PEDOT desirable. This can be achieved by lowering the surface tension of the formulation. In the shown example the surface tension was lowered from 32.5 dyne/cm to 25.5 dyne/cm, resulting in identical diameters and height profiles on both ITO and PEDOT (see Figure 7).

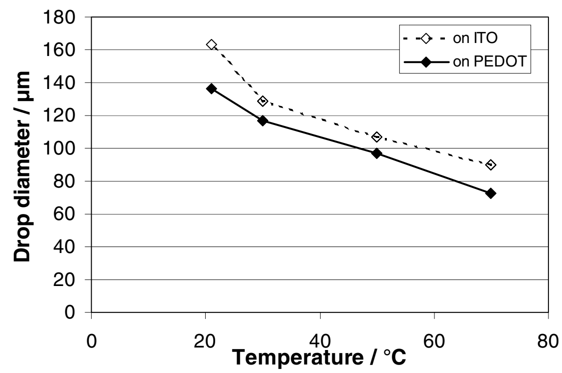

Figure 6: Diameter of drops on ITO and PEDOT for a formulation with 32.5 dyne/cm.

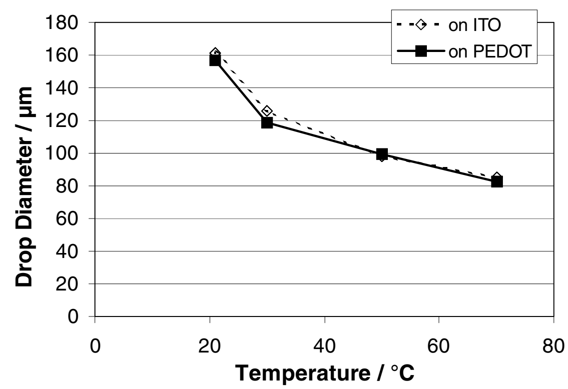

Figure 7. Diameters of dried drops for a modified formulation. The surface tension of the formulation was reduced to 25.5 dyne/cm.

Preparation of PLED Test Devices

As has already been mentioned, the materials development for RGB materials relies on the evaluation of PLED test devices that are commonly prepared by spin-coating. Inkjet formulations however, are often prepared in different solvents or are modified to change rheological properties, be it for wetting and the resulting film homogeneity or for reasons of sustainable jettability. The first test devices to check the influences of this new deposition method should therefore be relatively simple and as compatible to the spin-coating device structure as posssible. The substrate structure that was chosen consisted of small pixelated areas with 9x9 pixels each. The pixel area was 200x200µm² with a pixel pitch of 220µm, the height of the photo resist structure was 800nm. For these large pixels, it is better to print the low surface tension formulation at room temperature rather than at elevated temperatures because the improved wetting and reduced pinning provides a good flow to the edges of the pixel.

After cleaning, the devices were treated with ozone for 15 Minutes. Directly afterwards, a 20 nm layer of PEDOT was spin-coated onto the substrate to provide an even hole injection layer for the subsequent printing of LEP materials.

The LEP material was applied by printing lines of drops onto the active area of the device. The print head was tilted by 57.6° to align the projected nozzle pitch to the pixel pitch.

Assuming that one drop homogeneously fills one pixel, the resulting wet film is 1μm and the dry film thickness 13.8nm per drop. In order to obtain the desired film thickness of ~80nm, 6 drops every 200μm or 30 drops / mm are required. Due to accumulation of ink at the edges of the pixels, printing of 30drops / mm results in a film thickness of ~60nm at the center of the pixel. In order to increase the dry film thickness at the center of the pixels up to 80nm, 40drops / mm are necessary.

To prevent overflow of the material, the devices were printed in two successive runs. First, all odd columns were filled, and after drying, the even columns were printed. In order to guarantee identical printing conditions for the two runs, the remaining organic solvent from the first line must have evaporated before printing the second column. Otherwise the increased vapor pressure of organic solvent above the display during the second run leads to slower drying of the even lines and therefore to irregular odd and even columns.

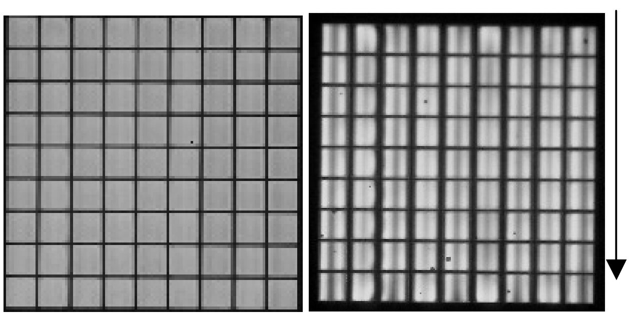

Figure 8. PL image (left) and EL image (right) of a device where the LEP material was deposited by ink jet printing. The arrow indicates the printing direction.

A common way to check the homogeneity of printed films is by photoluminescence (PL) microscopy. Figure 8 compares the PL and electroluminescence (EL) images of an inkjetted device that was printed acccording to the described procedure. The PL intensity distribution is more homogeneous than the EL intensity. This reflects the fact that for thin films the PL intensity is proportional to the film thickness. The EL reflects the radiative recombination of injected charge carriers under an applied electric field. Assuming that the electric current is only limited by the build up of space charges in the device, the current, and hence the EL intensity, is proportional to d^{-3}, where d is the thickness of the film (6). This dramatic dependence on the film thickness points out that the PL image alone is not sufficient to predict the homogeneity of the resulting EL image.

Conclusions

Ink jetting is a straightforward technique for the printing of structured PLED devices. The formulations for this technique must be adapted to the used print head, the substrate and the print strategy. Modifications in the surface tension of the formulations can lead to improved film homogeneity and changes in the interface to the underlying PEDOT. The preparation of working devices is necessary to judge the quality of the printing process since PL images are not sensitive enough to pick up the small inhomogeneities that can lead to a perceived unevenness in the brightness of the device.

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Biography

Juergen Steiger is physicist by education and received his master´s degree in the field of quantum optics from the University of Heidelberg in 1997. He received his PhD in Material Science in 2001 from the Technical University of Darmstadt for his research on charge transport in organic semiconductors and joined Covion Organic Semiconductors in April 2001. He is responsible for the testing of PLED inkjet formulations within the application laboratory.