P-181: Solution-Processed Full-Color Polymer-OLED Displays Fabricated by Direct Photolithography

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Abstract

For the first time a full-color display processed by direct photolithography is demonstrated. The solution-processed devices consist of stripes of red, green and blue emitting polymers which are sandwiched between electrodes in a passive-matrix geometry. In contrast to other approaches the photo-activated crosslinking-reaction used to pattern the emitter does not have a negative effect on the device-performance.

1. Introduction

Solution processed polymer OLEDs provide an attractive alternative to small molecule devices, mainly due to their significantly reduced production cost. Fabrication of small molecule OLEDs normally requires the use of vacuum deposition techniques which are relatively expensive, especially if large substrates are used. One advantage of using vacuum evaporation processes, however, is that the structuring of the emissive layer is achieved relatively easily with shadow masks. For solution processed polymers the situation is more complicated. Various techniques, such as different printing processes (ink-jet [1], screen printing [2], etc.), laser induced thermal imaging [3,4] or selective bleaching [5] have been proposed to define the required pixel structure in the emissive layer. Although these techniques are in principal compatible with the requirements for polymer OLED displays, they usually require extensive substrate-preparation, for example by local modification of the surface energy of the substrate or they have a negative impact on the performance of the material.

Here we demonstrate a different and potentially less expensive approach to define the required structures in layers of red, green and blue emitting polymers. Appropriate chemical functionalization of the emitting polymer is used to add photoresist-like properties to the material. We then employ conventional contact mask photolithography to selectively crosslink thin films of these polymers. Subsequent spin development with an organic solvent dissolves the non-cross-linked parts of the film (see Fig. 1).

Photolithography is a very common and mature technology in the electronics industry. Presently, resolutions below 100 nm are readily achieved; the fundamental resolution limit will be determined by diffraction effects. Additionally, photolithography is well suited for high volume production, especially if the resolution requirements are in the range of tens to hundreds of micrometers. In today's LCD display production the RGB color filters consist of dye doped photoresists and are routinely structured by lithography. Integration of the smart-resist process into large volume display production is therefore expected to be much easier than the adaptation of competing approaches.

In our previous work we have successfully used oxetane-functionalized triphenylamine-dimers (TPD) to form cross-linked and insoluble polymer networks which were used as hole transport layers in solution processed multilayer OLEDs [6]. Recently, we have also shown that electroluminescent polymers containing oxetane side groups can be structured photochemically with resolutions compatible to the requirements for full-color displays [7]. Here we extend this work on the basis of similar materials and demonstrate the first full-color RGB device with individually addressable pixels fabricated completely by direct photolithography.

2. Process Development

In order to add photo-resist like properties to the emitting polymers used in this work, oxetan side groups were attached to the polymer backbones through alkyl spacers. The general chemical scheme of the process used here was described

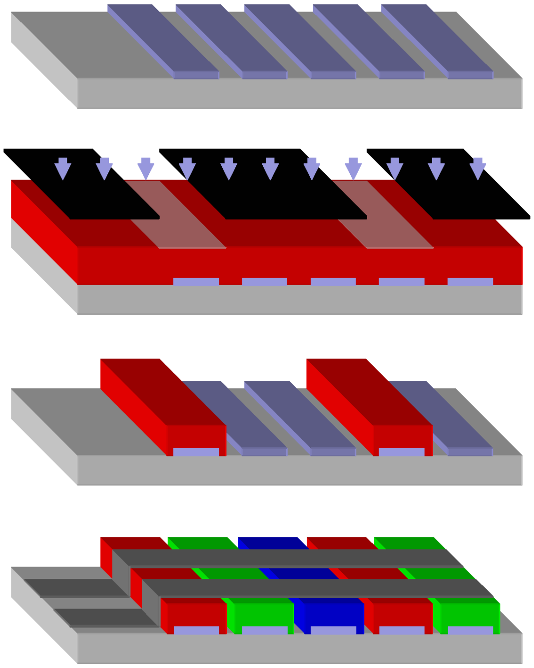

Figure 1: Schematic illustration of the direct photolithography process for the fabrication of a full-color display. The red emitting polymer is spin-coated onto the substrate with an ITO comb structure and selectively exposed to UV light using a contact mask-aligner. Subsequently, the non-crosslinked parts are dissolved and the procedure is repeated for the green and the blue emitter. Finally, cathode rows are deposited by thermal evaporation through a shadow mask.

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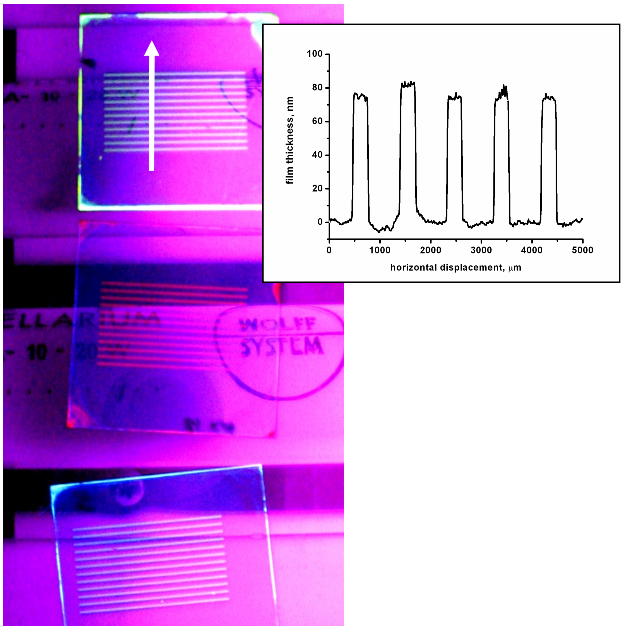

Figure 2: The photolithography process was optimized separately for the red, green and blue emitting materials. The fluorescence photograph shows samples with stripes of the different materials as required for a full-color display. Inset: Profilometer line scan along the white arrow in the photograph. Each line of the green polymer has a width of 300 µm, the spacing is 600 µm as required for the stripes of the two other colors.

previously [8]. Here we summarize the main features and discuss the relevant aspects for direct photolithography. Since oxetan groups are normally crosslinked cationically, the crosslinking can be selectively started by adding a photoacid such as {4-[(2-hydroxytetradecyl)-oxyl]-phenyl}-phenyliodonium hexafluoro antimonate to the polymer solutions prior to spin coating. When the spin coated films are exposed to UV light, the proton, donated by the photoacid, activates an oxetane ring for the attack of a second oxetane group. After a chemical bond is established, the remaining charge can attract other oxetane groups which leads to a chain reaction that eventually results in an insoluble network.

It has already been reported that the formation of an insoluble polymer network requires a “soft-curing” step (80 °C, 1 min) that provides sufficient diffusion mobility for the crosslinking reaction to penetrate through the entire film. However, since there is no defined termination reaction for the crosslinking process this can also result in undesired crosslinking in dark regions of the film. Therefore, a careful balancing of the different process parameters is essential to image small structures into the polymer films. The soft-curing temperature, the UV exposure time, the concentration of the photoacid and the concentration of oxetane groups were identified as the most influential factors.

Note that due to the self-sensitization of the material, very low UV doses were sufficient to achieve complete cross-linking. To achieve optimum resolution, the lithographic processing conditions were optimized for each polymer separately. To prevent undesired crosslinking in non-illuminated parts of the film, exposure doses below 50 µJ/cm^2 were required for the blue and the green polymers. The red emitting materials were found to require higher UV-doses (500 µJ/cm^2) but lower concentrations of photoacid (0.2 wt% rather than 0.5wt%) than the green and the blue emitting polymers. We explain this observation by the different energetic structure of the materials and by a reduced concentration of oxetane groups in the red emitting material. After process optimization we were able to transfer 2 µm sized features from a shadow mask to 80 nm thick polymer films with full depth-modulation and steep edges. As an example Fig. 2 shows a fluorescence photograph of samples with stripes of the three different polymers, all of them separately optimized as required for the full color display.

2. Device Fabrication

The general scheme of device fabrication is illustrated in Fig. 1. Lines of ITO electrodes with a width of 400 µm or 200 µm were structured on a glass substrate by conventional lithography. The substrates were then thoroughly cleaned in chloroform, acetone and water and by a 10 min UV ozon cleaning. Subsequently, a homogenous layer of PEDOT (Baytron P AL4083) was deposited by spin-coating and baked at 110 °C for 1 min to remove residual water. An additional polymer hole-transport layer (HTL) was deposited on top of the PEDOT layer to improve the device performance and stability. The HTL was also crosslinked via oxetane sidegroups to prevent dissolution of this layer in the following processing steps. No attempt was made to pattern the PEDOT or the HTL layer since conductivity estimations showed that cross-talk, resulting from a lateral current flow between adjacent rows and columns should be negligible.

Subsequently, the first emissive layer, e.g. red emitting, was spin-coated, then selectively cross-linked via UV-illumination, and finally developed with an organic solvent, removing the non-cross-linked parts of the film.

By repeating the procedure for the green and the blue emitting material, parallel stripes of red, green and blue emitter were formed on top of the ITO contacts. For practical reasons the lithographic process was carried out in air.

Finally, parallel metal stripes aligned perpendicularly to the underlying polymer/ITO stripes were evaporated as top contacts using ultra-fine shadow-masks.

We fabricated two generations of devices. Displays of the first generation (Gen1) contained ten rows and thirty columns, each pixel covered an area of 400 µm x 1200 µm. For the second generation (Gen2) we used a smaller pixel size (200 µm x 600 µm) and a device structure with 20x36 pixels.

3. Device Characteristics

The final devices were connected to a commercially available passive matrix driver (OC2 evaluation board, Fraunhofer IPMS, Dresden) operating in constant current mode. As can be seen in Fig. 3, each pixel can be addressed separately and a homogenous brightness level is achieved across the entire device. As expected, there is virtually no cross-talk between adjacent rows and columns. The displays also show good color saturation and the CIE color coordinates are in good agreement with the CRT standard as can be seen from Fig. 4 (CIE R = 0.68, 0.32, G = 0.29, 0.59 and B = 0.17, 0.20).

The IVL characteristics were measured for individual columns of differently colored pixels in a conventional OLED test stand. The current-voltage characteristics are well behaved without any sign of parasitic leakage currents. The performance of the devices

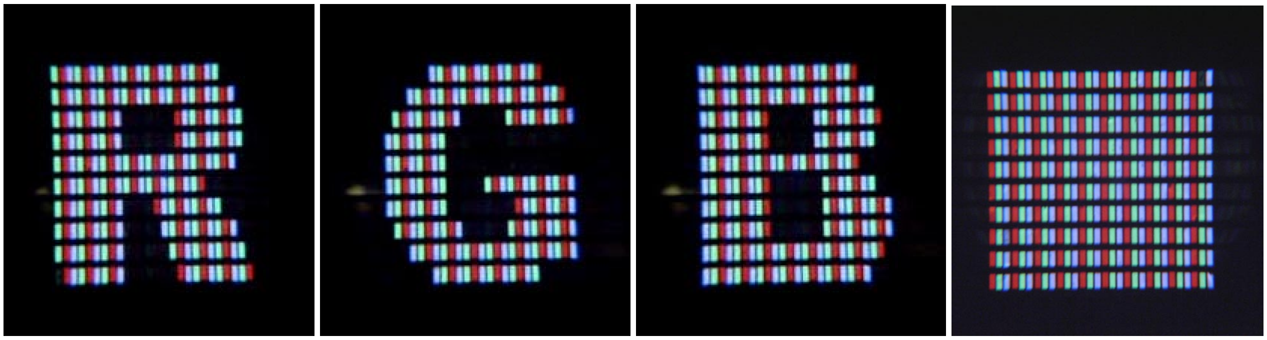

Figure 3: Test pictures displayed on the full-color RGB display fabricated by the smart photo-resist approach. The photographs show Gen1 displays, the pixel size is 400 µm x 1200 µm.

compares favorably with state-of-the-art fluorescent polymer OLEDs. The onset voltage is in the range of 3-4 V. Efficiencies of 7.7 Cd/A, 4.1 Cd/A and 2.3 Cd/A were achieved for green, blue and red, respectively.

4. Summary and Outlook

In summary, we have fabricated a full color passive matrix OLED display using direct photolithography. Oxetane sidegroups allow selective crosslinking of the electroluminescent polymers and provide for the smart photoresist properties of the materials used in this work. The devices discussed here were characterized by homogenous brightness levels across the entire display area, good color saturation of the red, green and blue subpixels and reasonable efficiency.

Note that due to the good stability of the devices even at high current densities we decided to demonstrate the feasibility of the smart photoresist approach using a passive-matrix driving scheme. In the future, active-matrix backplanes will be used to increase the number of addressable pixels and the lifetime of the devices.

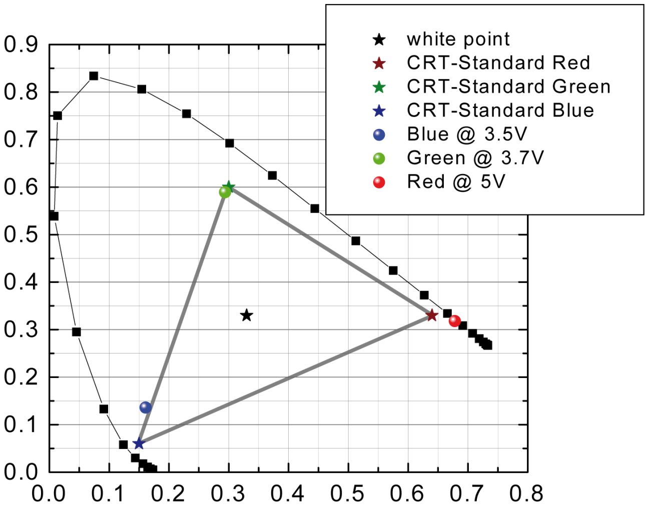

Figure 4: CIE coordinates of the red, green and blue emitters in the final display. The coordinates were calculated from the electro-luminescence spectra that were measured in the final device with all red, green or blue subpixels switched on.

Since the process proposed here did not cause a reduction of the device performance (compared to non-crosslinked reference devices), we believe that direct photolithography is a very promising technology for future OLED display production.

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