White multi-layered polymer light emitting diode through matrix assisted pulsed laser evaporation

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The development of alternative deposition techniques is crucial for several types of soft semiconductor: the conjugated polymeric compounds. In this case a new deposition method would be an important step towards the fabrication of low cost multi-layered organic light emitting diodes suitable for display or lighting applications. In this context, we have investigated a white light-emitting polymeric hetero-structured diode consisting of three stacked blue, red and green light emitting polymers. In order to circumvent the issue of selecting orthogonal solvents in solution-deposition approaches, we combined spin-coating with a matrix-assisted pulsed laser evaporation (MAPLE) technique (see Fig. 3), resulting in the realization of a polymeric multi-layered stack. Recently, the Matrix Assisted Pulsed Laser Evaporation (MAPLE) technique has prompted interest as an alternative route to the conventional deposition of polymers. The important advantages of the MAPLE approach as compared with solution cast techniques are: (i) punctual control of thickness, (ii) the ability to deposit multilayers and (iii) thin film deposition on non-planar substrates with good surface coverage. In addition, the energetic ablation mechanism exploited by MAPLE represents a valid alternative for polymer deposition, since thermal evaporation cannot be used.

In this research activity we present a white PLED structure that combines spin-coating and MAPLE for the deposition of three stacked layers consisting of blue (BP), red (RP) and green (GP) light-emitting polymers. The proposed hybrid technique circumvents the overall problems mentioned above, thus allowing for the realization of active multi-layer polymeric-based devices emitting white light without the need for thermal treatment and orthogonal solvents. This demonstrates that MAPLE is useful and reliable for fabricating white organic LEDs, which is a challenging benchmark for PLEDs, and opens the way to reduce the gap between Polymer LEDs and Small Molecular OLEDs.

By carrying out AFM measurements, a RMS-surface roughness of about 1 nm was achieved for the BP indicating that the material is extremely processable through spin-coating. After the MAPLE deposition of the other layers, the mean roughness value increased to 6.9 - 0.9 nm for the bilayer device (BP + RP) and to 10.3-1.6 nm for the complete three-layer (BP + RP + GP) polymeric stack (see Fig. 2). However, these roughness values are still compatible with OLED fabrication

The Electro Luminescence (EL) emission of the three-layer polymeric stack with MeOTPD as a spacer is reported in Fig.2; the EL spectra of the single layer devices deposited using spin-coating are also reported for comparison. Also, it is important to notice that the electroluminescence contribution of the green and red polymers, deposited using MAPLE in the three-layer stack, significantly match with the corresponding spin-coated material emission. As the red emitting layer acts as a trap for the carriers due to the deeper position of the HOMO and LUMO levels, the deposition of a few nanometers of MeOTPD between the RP and GP layers allows for fine control of the red light emission, thus resulting in a well-balanced white light electroluminescence as well as in PL. MeOTPD is a hole conductive material and acts as a filter for electrons but not for holes and it does not absorb any emitted light due to its large energy gap.

By controlling the carriers and the energy transfer across the three light emitting layer interfaces, as well as the interplay between the deposition parameters, a pure white colour emission (photoluminescence spectrum in Fig3b) with Commission Internationale de l'Éclairage coordinates of (X = 0.327, Y = 0.374) and a Color Rendering Index of 70 has been achieved. Our study represented the first proof of a light emitting diode made with multi-layer polymeric thin films emitting white light.

The maximum luminance shown by the white OLED is about 200 cd/m2, which is good for display applications. We ascribe this limit to the red emitting compound which shows a similar behavior, while the blue and green light emitting polymers show luminance compatible with lighting (4500 cd/m2). Additional studies have to be carried out to improve these performances by choosing more efficient polymers. This is beyond the scope of this work where the reliability of multi-layer polymeric structures

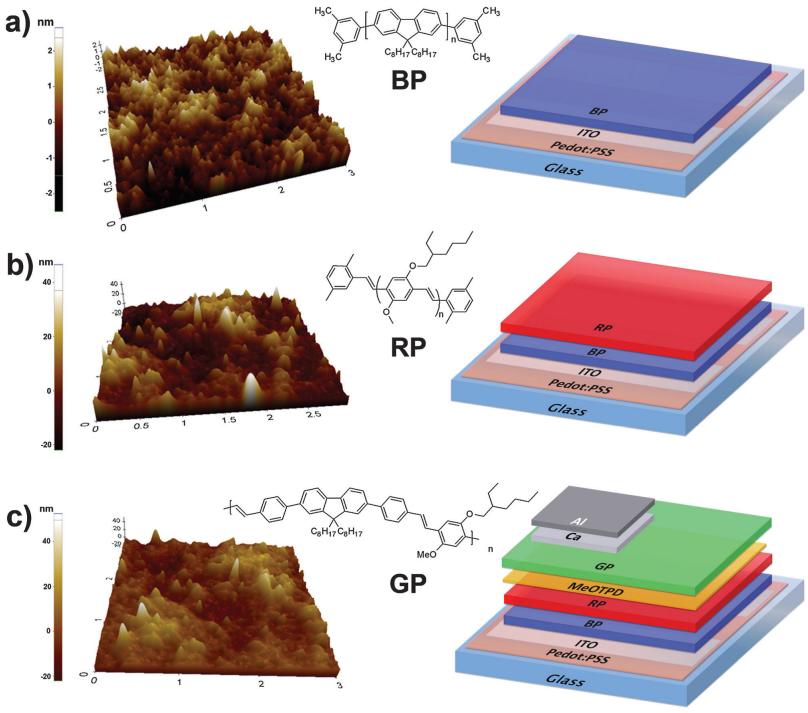

Figure 1. Atomic force microscopy images and related schemes of the layers deposited onto the ITO/PEDOT layers BP + RP, (c) BP + RP + GP with MeOTPD as a spacer. The chemical structures of the green (GP), blue (BP) and red (RP) polymers used in this work as emissive layers are also reported.

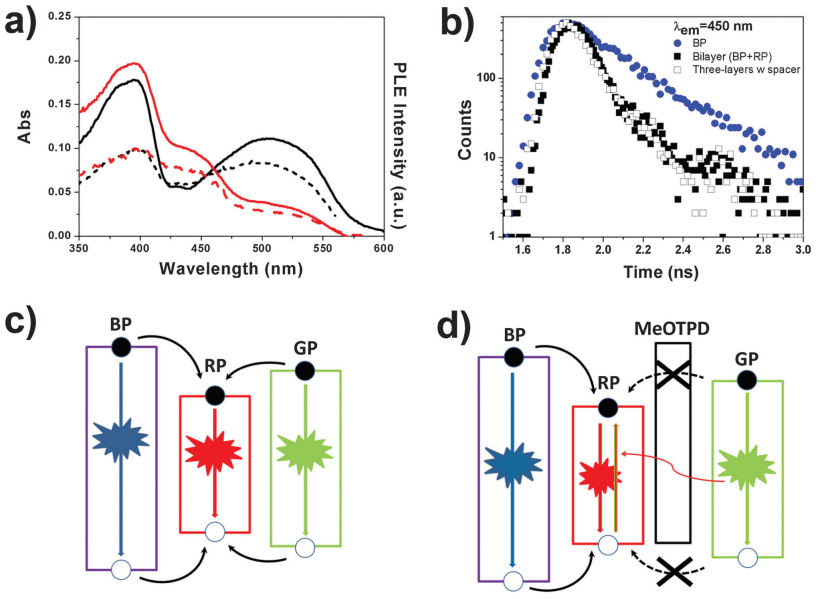

Figure 2. Working principle and deposition setup of MAPLE technique. b) PL spectra of the Blue Polymer (blue line), Green Polymer (green line) and Red Polymer (red line) deposited through spin-coating (dashed lines) and MAPLE (solid lines). PL white emission (black line) from the three-layer stack (BP + RP + RP).

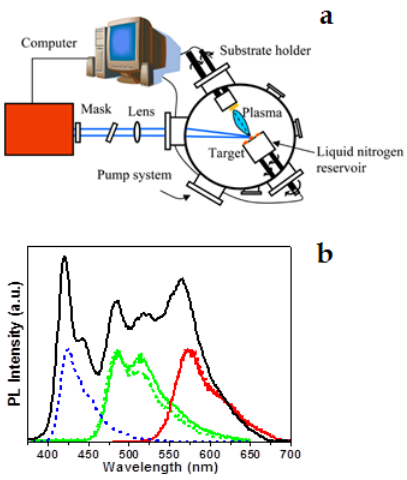

Figure 3. Exciton transfer mechanism in the three-layer structure. Exciton transfer mechanism in the three-layer structure with a 2 nm thick MeOTPD spacer between the RP and GP layers. The presence of MeOTPD reduces the probability of exciton transfer from the GP to RP at their interface, thus the most probable way to excite the RP is via the emission from the GP and the re-absorption by the RP layer.

was demonstrated as a proof of concept. A further reason for the relatively higher voltage of the white device, compared to the blue and green spin-coated ones, is the film matching between the different polymers. Although the roughness reported for the MAPLE deposited polymer films is low and is among the best reported in the literature for this kind of deposition technique, there could not be optimum matching among the whole area, determining leakages and lowering of the performances. This effect, related to the film interfaces, is under investigation.