Para-Sexiphenyl Based OLED Devices Grown on Light Sensitive Polymer Substrates

C. Simbrunner¹, G. Hernandez-Sosa¹, T. Höfler², G.Trimmel², W. Kern^{2,3}, and H. Sitter¹

¹ Institute for Semiconductors and Solid State Physics, Johannes Kepler University Linz, Altenbergerstrasse 69, 4040 Linz, Austria

² Institute for Chemistry and Technology of Organic Materials, Graz University of Technology, Stremayrgasse 16, A-8010 Graz

³ Departement of Chemistry of Polymeric Materials, Franz-Josef-Straße 18, A-8700 Leoben

We report on OLEDs based on Para-sexiphenyl (PSP), which has been deposited by Hot Wall Epitaxy (HWE) on Polynorbornene, a photosensitive polymer. The used substrates have been pre-patterned by UV illumination leading to a changed surface polarity and consequently to an induced change of morphology and crystalline properties of the grown PHP. In particular we report on the optical properties of the devices which can be tuned by UV illumination of the polynorborene substrates.

Introduction

Morphology and crystalline order is determining for improving the electrical and optical properties of organic films. Therefore it is of great importance to study the growth kinetics of organic materials on substrate surfaces with well controlled properties. Parasexiphenyl (PSP) ($C_{36}H_{26}$), a six units oligomer of para-phenylene, is a promising candidate as an electro active layer in organic LED displays due to its blue luminescence with high quantum yield [1], [2]. Moreover, it is classified as a wide gap organic semiconductor with an electronic band gap of 3.1 eV with photoluminescence in the blue visible range and polarized absorption and emission when provided in well ordered films [3].

The Hot-wall epitaxy (HWE) technique offers the advantage that it works close to thermodynamic equilibrium. Therefore it allows organic molecules to find the most suitable arrangement into the crystal lattice and as a consequence, highly ordered organic thin films can be obtained [3], [4]. Organic thin films grown by HWE have shown outstanding optical and electrical properties [5], [6]. Extensive morphological and structural characterization has been already performed on HWE grown PSP films deposited on various substrates such as KCI and muscovite mica, showing that the nature of the substrate and the growth conditions are ruling parameters for the molecular packing of the films [7].

In the presented work, an amorphous polymer poly(diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (PPNB) containing photoreactive aryl-ester groups was chosen as substrate. Upon illumination with UV-light of λ < 280 nm these ester groups isomerize to the corresponding hydroxyketones in the so-called photo-Fries reaction [8], [9]. Recently, we have shown that the photoreaction in PPNB yields up to 21 % hydroxyketones as photoproducts [10]. The UV-induced reaction leads to a large increase of the refractive index as well as of the surface polarity. This enhanced polarity and the generated new functional groups can be used for selective post-modification reactions [11]. In particular we report on the optical properties of the devices which can be tuned by UV illumination of the polynorborene substrates.

Experimental Methods

Sample Preparation

The procedure to synthesize PPNB is reported by T. Höfler et al [10]. For the substrate preparation a 10 mg/ml solution of PPNB in CHCl₃ was prepared and stirred for 12 h. Then the solution was spin cast onto Glass/ITO/PEDOT:PSS-substrates resulting in 80 nm film thickness (see Fig. 1). In order to provide equivalent growth conditions for UV-exposed and non-irradiated surfaces, each substrate was divided in two regions. One half of the substrate was exposed for 20 min to UV light (254 nm) while the other half was protected from UV illumination. The unfiltered light of an ozone-free mercury low pressure UV lamp (Heraeus Noblelight; 254 nm) was used. The illumination-process was done in inert gas atmosphere (nitrogen with a purity >99.95%) in order to avoid unwanted oxidation reactions.

After the illumination process the substrates were transferred via a load lock to a HWE growth chamber working at a dynamic vacuum of 9x10⁻⁶ mbar. A 15 min in-situ preheating procedure was applied in order to reduce surface contaminations. The substrate temperature during preheating is chosen the same as the growth temperature in order to allow constant thermal conditions during the whole deposition process. The working principles of a HWE system can be found elsewhere [12].



Fig. 1: Schematic of the sample preparation. After UV illumination process the sample is transferred to the HWE system where PSP is evaporated. Finally AI contacts are created by thermal evaporation

After the deposition of PSP on top of the described sample structure AI contacts were deposited by thermal evaporation. Contacts were structured by using a shadow mask providing contact pads on the illuminated, non-illuminated and at the interface in between the two domains.

In order to provide electrical contact to the sample, gold wires were indium-soldered to the contact pads. The whole structure was then mounted on a chip carrier, providing a flexible solution for the next measurement steps.

Measurements

All samples were measured using a Keithley 2400 I-V-Source unit which is synchronized with an Avantes fiber spectrometer. Consequently I-V characteristics of the OLED's can be acquired parallel to electroluminescence emission spectra. In that way the CIE color-coordinates, the spectral response as a function of applied current and the I-V characteristic can be determined. A detailed analysis of the spectral response is reported elsewhere [13].



Fig. 2: Optical photograph of a PPNB-PSP-OLED structure showing the device without applied voltage (a) and during operation (b). The line indicates the border between illuminated and non-illuminated substrate regions. In section (c) typical IV curves for both domains are depicted.

In order to provide optical images of the fabricated device an optical microscope equipped with a standard digital camera was used. Typical results are depicted in Fig. 2 showing an OLED device without applied voltage (a) and during operation (b). Striking seems that no obvious structural difference is noticed between illuminated and non-illuminated part of the samples as depicted in Fig. 2 (a). The border line of the two regions is indicated by a black line splitting the tested contact pad in two parts. Nevertheless during operation a huge effect is visible showing a clear blue emission of the not illuminated part, whereas the UV treated region stays dark. A more detailed analysis of

the effect is given by electrical measurements, using two geometrical identical contact pads situated on the illuminated and the non-illuminated part of the sample. Typical results are shown in Fig. 3 (c) indicating a change in conductivity due to the UV-illumination by a factor of 5 - 10.

Conclusion

In conclusion the presented structuring method represents a powerful tool in order to provide structured OLED devices. It was demonstrated that by UV illumination of the substrate the optical properties of a device can be controlled opening new perspectives for OLED pre-structuring processes. Nevertheless more detailed investigations have to be done to explain the presented effect in more detail.

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