

Epitaxially-Grown Oxadiazole Layers for Light Emitting Diodes

R. Fan[α], M.J. Turon[α], J.E. Langseth[α], G.G. Malliaras[α], S. Gu[β], L. Sukhomlinova[β] and R.J. Twieg[β]

[α)]Department of Materials Science and Engineering, Cornell University, Ithaca, NY

[β)]Department of Chemistry, Kent State University, Kent, OH

Abstract

We use a simple epitaxial growth technique to prepare oriented layers from a liquid crystalline oxadiazole derivative. The high degree of molecular orientation in these layers is found to lead to a dramatic enhancement in the electrical characteristics of organic light emitting diodes.

Keywords: charge transport, electroluminescence, liquid crystals, orientation.

Introduction

Organic light emitting diodes (OLEDs) are attracting considerable interest for applications in flat panel display technologies[1]. Both small molecules and polymers are currently being investigated. The operation of OLEDs involves charge injection from metal electrodes, transport in the organic layer(s) and radiative recombination[2]. In the most efficient OLEDs, injection from Ohmic contacts provides the organic bulk with space charge limited current and the parameter that limits performance (in terms of operating voltage) is the carrier mobility in the organic[3].

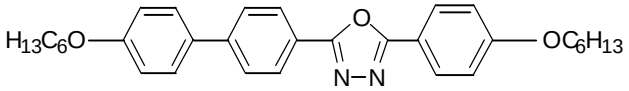

Figure 1. Chemical structure of HOBP-OXD.

Liquid crystalline (LC) materials with (electronic) charge transport properties are recently attracting a great deal of attention due to their very high mobilities[4-6]. The latter result from the high degree of intermolecular order in the liquid crystalline state. Therefore, the introduction of liquid crystalline materials in OLEDs seems to offer the opportunity to increase device performance[7-8]. Orientation of the LC molecules is induced by surface alignment layers (usually a rubbed polyimide). This process takes place in one of the liquid crystalline phases, which for these molecules usually occur at elevated temperatures[7-8].

In this paper we use a simple epitaxial growth technique to prepare oriented electron transport layers without the use of additional alignment layers. We use the liquid crystalline oxadiazole derivative HOBP-OXD (chemical structure shown in figure 1), which is crystalline at room temperature and therefore allows the fabrication of organic light emitting diodes using vacuum deposition techniques. We investigate the influence of molecular orientation on the OLED electrical characteristics.

Experimental

The synthesis of HOBP-OXD has been reported in a previous publication[9]. The devices were made by subsequent deposition of 15nm of copper (II) phthalocyanine (CuPc), 60 nm of *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD) and HOBP-OXD on ITO covered glass substrates at 10^{-6} mbar. The device fabrication was completed by the deposition of 20 nm thick Ca cathodes, overcoated with 20 nm Al. The active device area was $3mm^2$. The electrical characteristics were measured with a 236 Keithley source-measure unit and the radiance with a calibrated Si detector. The spectral characteristics of the diodes were measured with an Ocean optics fiber spectrometer. The device fabrication and characterization steps took place inside a nitrogen glove box with 1ppm or less oxygen and moisture contents. The optical density of the films was measured with a Perkin-Elmer spectrometer.

Results and Discussion

Oriented layers of rod-like molecules can be obtained by a simple epitaxial growth technique[9-10]. According to this technique, a thin organic layer (of the order of 5 nm) is deposited first, then taken out of the evaporation chamber and gently rubbed a few times in a fixed direction with a velour cloth. Subsequent deposition the rest of the organic produces a film with a high degree of molecular orientation. This is shown in figure 2, where the optical density of two films is compared. The figure shows the optical density measured at 320nm using linearly polarized light incident along the sample normal as a function of (azimuthal) sample rotation. The filled circles are for a

sample that was oriented using this rubbing technique, while the open circles are for a control sample prepared side-by-side but not rubbed. The light absorption reaches its highest value when the oriented sample is positioned with the rubbing direction parallel to axis of the polarizer (0 and 180 degrees) and reaches its lowest value for perpendicular orientation (90 and 270 degrees). In contrast, the control film shows very little dependence of its optical properties on orientation.

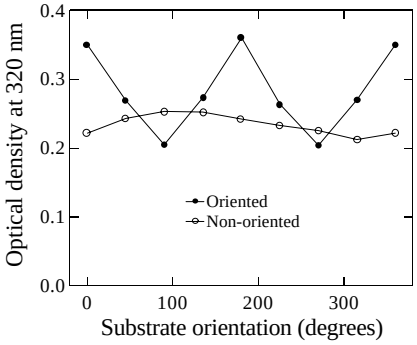

Figure 2. Absorption of polarized light from two HOBP-OXD samples as a function of sample rotation.

In figure 3, polarized optical microscopy images are shown for the control (left) and the oriented (right) sample. The white bar on the right picture indicates the rubbing direction. The presence of crystalline regimes, oriented along the rubbing direction, is clearly seen in the epitaxial sample. On the other hand, the control sample appears to be isotropic.

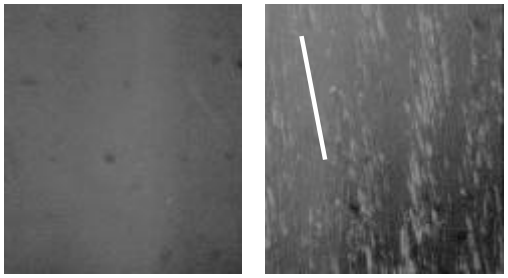

Figure 3. Polarized optical microscopy pictures of the control (left) and the oriented film. The white bar indicates the rubbing direction.

Since oxadiazoles are electron transport species, organic light emitting diodes were fabricated in a bilayer configuration, using TPD as the hole transport layer. CuPc was introduced to enhance hole injection from the anode (ITO). The electrical characteristics of two devices, one with an oriented oxadiazole layer and one with an isotropic one, are shown in figure 4. The device with the isotropic layer exhibits low current and no rectification. The device with the oriented layer, on the other hand, exhibits substantially higher current and an order of magnitude rectification at 5 V. Orientation of the HOBP-OXD molecules and the resulting increase in the degree of crystallinity is clearly improving the layer's electron transport properties, leading to better device characteristics.

Blue light emission was observed from both the device with the isotropic and the oriented HOBP-OXD layer. We are currently measuring the device quantum efficiency as a function of the HOBP-OXD layer crystallinity.

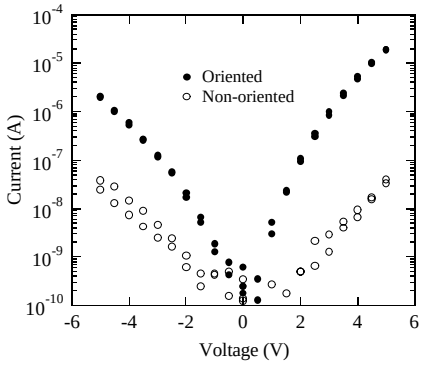

Figure 4. Electrical characteristics of OLEDs with oriented and isotropic HOBP-OXD layers.

Conclusions

In conclusion, we have used a simple epitaxial growth technique to prepare oriented electron transport layers from HOBP-OXD. Organic light emitting diodes were fabricated using these layers. Molecular orientation was found to lead to a dramatic enhancement in the device electrical characteristics.

References

1. G. Lüssem, J.H. Wendorff, *Polym. Adv. Technol.* **9**, 443 (1998).
2. S. Miyata, H. S. Nalwa, Eds., *Organic Electroluminescent Materials and Devices*, Gordon and Breach, Amsterdam, (1997).
3. G.G. Malliaras, J.R. Salem, P.J. Brock, J.C. Scott, *Phys. Rev. B.* **58**, R13411 (1998).
4. D. Adam, P. Schumacher, J. Simmerer, L. Haessling, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* **371**, 141 (1994)
5. M. Funahasi, J. Hanna, *Adv. Mat.* **78**, 2184 (1997).
6. H. Tokuhisa, M. Era, T. Tsutsui, *Adv. Mat.* **10**, 404 (1998).
7. H. Tokuhisa, M. Era, T. Tsutsui, *Appl. Phys. Lett.* **72**, 2639 (1998).
8. K. Kogo, T. Goda, M. Funahashi, J. Hanna, *Appl. Phys. Lett.* **73**, 1595 (1998).
9. R. Fan, D. Culjkovic, P. Piromreun, M.J. Turon, J.E. Lnagseth, G.G. Malliaras, S. Gu, L. Sukhomliniva, R.J. Twieg, to appear in *SPIE proc.***3797** (1999).
10. M. Era, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* **67**, 2436 (1995).

Biography

Malliaras studied Physics at the Aristotle University (Greece) and did his doctoral research in the University of Groningen (the Netherlands), on photorefractivity in polymers. Before joining the faculty at Cornell in July 1998, he was a post doctoral fellow at the University of Groningen ('96) and the Center for Polymer Interfaces and Macromolecular Assemblies (CPIMA), at the IBM Almaden Research Center ('97-'98). His research focuses on the design, fabrication, characterization and computer modeling of organic optoelectronic devices such as light emitting diodes and photovoltaic cells. He is a member of the American Physical Society and the Materials Research Society.