

Synthetic Metals 127 (2002) 267-271



www.elsevier.com/locate/synmet

Polymer multilayer systems for electronic applications

H. Krüger, A. Wedel^{*}, S. Janietz

Fraunhofer-Institute of Applied Polymer Research, Geiselbergstrasse 69, D-14476 Golm, Germany

Abstract

For polymer electronic applications, it is important to use multilayer structures with conjugated polymers. For this reason, modified polymer structures were synthesized. The cyclovoltammetric measurements allows us to estimate the HOMO and LUMO energy levels of the synthesized materials. This knowledge is necessary for the development of efficient components like polymer light emitting diodes, polymer diodes and transistors. The characterization of such devices by current–voltage and brightness–voltage measurements will be described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Conjugated polymers; PLED; Cross-linking; Multilayer system; Electroluminescence

1. Introduction

Normally all conjugated polymers show a comparable solubility in organic solvents. It is known that multilayer structures with different conjugated polymers are difficult to realize because the solubilization of the first polymer layer cannot be hindered efficiently during the next spincoating step. Here, we present a way to overcome this problem. The polymers, we used for multilayer structures, were hole transport materials like thianthrene containing polyimide or cross-linkable, alkoxy substituted poly-(pphenylenevinylene copolymers) and a dialkoxy substituted poly(p-phenylene-1,3,4-oxadiazole) as electron transport material. To prevent solubilization, we convert the first polymer layer after spin-coating by thermal treatment to an insoluble cross-linked form. So, a second polymer layer can be spin-coated without any solubilization of the previous one.

2. Experimental

The hole transport material (PTPA) was obtained by thermal treatment of the soluble precursor polyamide. The polyamide was synthesized from diamino thianthrene and pyromellitic dianhydride in dimethyl acetamide (see Fig. 1). The polyamide solution was spin-coated on the substrate. After that the thermal conversion of the soluble

fax: +49-331-5693910.

polyamide to the insoluble polyimide took place at 200 $^{\circ}$ C under vacuum condition. The completeness of the imidization step was checked by Fourier transform infrared spectroscopy (FTIR) [1].

Another hole transport and orange emitting material is the well-known organosoluble poly(2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene) (MEHPPV). To realize insolubility of the spin-coated MEHPPV layer, we modified the polymer structure by copolymerization with a cross-linkable comonomer. Therefore, we synthesized diallyloxy or dicitronellyloxy substituted 1,4-bis(chloromethyl)-benzene derivatives. Statistic alkoxy substituted poly-(p-phenylenevinylene copolymers) (COMEHDAPPV) which are satisfying soluble up to a comonomer content of 30% per mole (see Fig. 2) were prepared by copolymerization of the 2-methoxy-5-(2'-ethylhexyloxy)-1,4-bis(chloromethyl)-benzene and the diallyloxy or dicitronellyloxy substituted 1,4-bis-(chloromethyl)-benzene following a modified Gilch procedure (dehydrohalogenation polymerization) [2,3]. The copolymer layers can be cross-linked by thermal treatment at 150 °C in a nitrogen atmosphere using a glove box system in which the oxygen and water content are below 1 ppm. So, it was possible to realize insoluble thin layers by the introduction of allyloxy or citronellyloxy side chains to the PPV-backbone which are stable during further spin-coating steps.

As electron transport material, we used a soluble thermostable 2,5-dialkoxy substituted poly(phenyl-1,3,4-oxadiazole) (PODH) (see Fig. 3). The synthesis was described elsewhere [4,5].

The PODH-layer was obtained by spin-coating toluene solutions with 0.5-1% by weight on the hole transport layer.

^{*}Corresponding author. Tel.: +49-331-5681910;

E-mail address: wedel@iap.fhg.de (A. Wedel).



Fig. 1. Synthesis of the thianthrene containing polyimide (PTPA).





Fig. 2. Structure of the cross-linkable poly(2-methoxy-5-(2'-ethylhexy-loxy)-*p*-phenylenevinylene)-co-(2,5-dicitronellyloxy-*p*-phenylenevinylene) (COMEHDAPPV, n = 0.7; m = 0.3).

Fig. 3. Structure of soluble poly[2',5'-bis(2'-ethylhexyl)-1,4-phenylene-1,3,4-oxadiazol-2,5-diyl].



Fig. 4. Brightness-voltage behavior of MEHPPV and COMEHDAPPV single layer devices.



Fig. 5. Spectra of EL and PL of different single (MEHPPV and COMEHDAPPV) and the double layer device of COMEHDAPPV and PODH.

3. Results

3.1. PLED

The typical structure of an electroluminescence device or of a polymer transistor can be described as an metal– polymer/(polymer)–semiconductor interface. We have found that the single layer devices with the MEHPPV and our copolymer COMEHDAPPV have the same brightness (about 200 cd/m² at 6 V), but different onset voltages (Fig. 4). For effective hole injection, ITO-electrodes (thickness 20 nm, resistance $<15 \Omega$ /square) on glass substrates were used. The thickness of the polymer layers were between 90 and 110 nm. The thicknesses of the electron injection contact were 30 and 100 nm for calcium and aluminum, respectively.

Double layer devices were realized using the hole transport material (COMEHDAPPV) and the electron transport material (PODH). The electroluminescence spectrum of the double layer (Fig. 5) was very broad because of the influence of the recombination in the electron transport layer.



Fig. 6. Typical transistor structure with a double layer system. Energy level scheme for an ITO/PTPA/Al/PODH/Al double layer structure. Values are calculated in electronvolts vs. vacuum level.



Fig. 7. Current-voltage behavior of a bilayer system of a polymer transistor.

The second layer (PODH) gives an additional emission part of the electroluminescence spectra of the whole device. These facts have recognized already to the photoluminescence of the material (maximum at 460 nm). The recombination of the charge carriers takes place in the vicinity of the interface between the hole transport and electron transport layer. We have found (Fig. 5) that the double layer device COMEHDAPPV/PODH have a nearly white emission with a brightness of about 300 cd/m² at 16 V (CIE color coordinates: x = 0.42, y = 0.40). No change in color was observed with applied voltage.

3.2. Diodes and transistors

We investigated the current–voltage (I-V) characteristics for testing the diode character of different single and multilayer structures to describe the function of such devices. To realize a bipolar diode structure, it was necessary to combine p- and n-type materials.

The reduction and oxidation peak potentials obtained by cyclovoltammetric measurements [6] of thin layers gave the possibility to estimate the LUMO and HOMO energy levels of the PTPA and PODH. These values are described in Fig. 6. From these values, follow that the electrical barrier between the ITO-electrode to the PTPA layer is with 0.7 eV not too high for the injection of holes. The electron affinity of 2.8 eV of the PODH material allows the electron injection from the Al-electrode into the polymer material. The Baytron layer (Bayer AG) was used as hole transport material to adapt the work function of the ITO-electrode to the PTPA layer. The aluminum electrode between the two polymer layers is

geometrically configured to control the current over the whole device by a separate voltage.

The current–voltage curves of the double layer systems are shown in Fig. 7. The onset voltage of the whole device can be controlled via a bias voltage between the first layer (PTPA) and the ground electrode (ITO).

Fig. 7 shows the switching behavior of the bilayer device. At different onset voltages the system switches from the non-conducting to the conducting state. That is only the switching behavior of the transistor. For fully transistor applications, we want to amplify the current of the device by the driving electrode.

4. Conclusions

We have prepared multilayer devices sandwiched between ITO and different metal electrodes. In this case, it is necessary to cross-link the first polymer layer. Single layer devices of OLEDs can only emit at special wavelengths. We found that in bilayer devices the electroluminescence can be controlled by thickness optimization of the different emitting layers up to white emission. A transistor structure with p- and n-type conjugated polymers was developed which can be used in the future for driving of PLEDs.

Acknowledgements

The authors are indebted to Franziska Küchler and Kristin Arlt for technical support and wish to thank the German Federal Ministry for Research and Technology within the research project No. 01 BK 916-919 for financial support.

References

- [1] R. Friedrich, Discussion, Freie Universität, Berlin, 1998.
- [2] H.G. Gilch, J. Polym. Sci., Part A 4 (1966) 1337.

- [3] H. Becker, H. Spreitzer, K. Ibrom, W. Kreuder, Macromolecules 32 (1999) 4925.
- [4] S. Janietz, A. Wedel, R. Friedrich, S. Anlauf, Polym. Prepr. 40 (1999) 1219.
- [5] S. Janietz, S. Anlauf, A. Wedel, Synth. Met. 122 (2001) 11.
- [6] S. Janietz, D.D.C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran, E.P. Woo, Appl. Phys. Lett. 73 (1998) 2453.