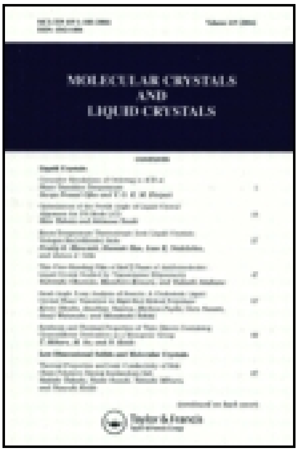

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Polyaniline Bilayer Composite Electrode for Efficient Polymer Light Emitting Diodes

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Version of record first published: 04 Oct 2006.

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 537–542
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POLYANILINE BILAYER COMPOSITE ELECTRODE FOR EFFICIENT POLYMER LIGHT EMITTING DIODES

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Abstract We reported that by using a combination of polyaniline (PANI) and Indium/tin oxide (ITO) as the transparent anode of a polymer light emitting diode with poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), (MEH-PPV), as the active layer, device performance can be significantly improved. The operating voltage can be reduced by ~ 30-50%, and the quantum efficiency can be increased by ~ 30-40% with respect to the devices using ITO alone as the hole-injecting anode. The barrier height at the PANI/MEH-PPV interface is estimated to be ~ 0.08-0.12eV, approximately half of that at the ITO/MEH-PPV interface.

INTRODUCTION

As a result of the significant processing advantages, mechanical advantages, size (area) advantages and the broad spectral range (color) of devices fabricated from semiconducting electroluminescent polymers,[1-9] there is growing interest in polymer light emitting diodes (LEDs) for use in display applications. Nevertheless, the efficiencies of such devices remain far below the theoretical limit. Since the active luminescent layer is a semiconducting polymer, mechanically flexible LEDs are possible. Such "flexible LEDs" were demonstrated[9] by using low surface resistance films of the metallic form of polyaniline as the transparent, hole-injecting electrode.

Parker[10] has shown that the polymer LED devices fabricated from poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) operate as tunnel diodes. The electronic bands of the semiconducting polymer can be assumed to be rigid as a consequence of the very low dopant concentration ($< 10^{14}$ cm^{-3}). The highest occupied molecular orbital (HOMO) of MEH-PPV is 4.9eV below the vacuum, while ITO has a work function of ~ 4.7eV [10], implying that an 0.2eV barrier is formed at the anode. The lowest unoccupied molecular orbital (LUMO) of MEH-PPV is 2.8eV below the vacuum level, so that a barrier of height 0.1 eV forms at the MEH-PPV/Ca interface (work function of Ca ~ 2.9eV). The tunnel diode model of the polymer LED predicts that the charge injection could be significantly enhanced if the barrier height of the polymer/metal contact were reduced. We have found that using polyaniline (PANI) as the anode material gives a ~ 0.1eV barrier height at the PANI/MEH-PPV interface (approximately half that of the ITO/MEH-PPV interface), consequently improving hole injection into the polymer LED.

EXPERIMENTAL

The LEDs discussed in this paper were three-layer devices, consisting of a conducting anode layer, a polymer active layer, and a metal cathode layer. For this study, Ca and Cu were used as the cathode, and PANI was used as anode. In order to avoid significant voltage drop in the electrode, it is desirable to decrease the surface resistance of the anode to less than about 100 ohms/square. Although this can be achieved using a thicker layer (>2500Å) of PANI, the transmittance of such a PANI electrode is less than 70%, which would lead to a 30% loss in external quantum efficiency. One possible solution to this problem is to over-coat an ITO electrode with a very thin layer (< 600Å) of PANI. We have found that a 600Å layer of PANI has a peak transmittance (~ 500nm) around 90%, while the ITO/PANI combination has a work function similar to that of PANI alone. Although the surface resistance of the 600Å PANI layer is higher than 600 ohms/square, the composite bilayer electrode has a surface resistance below that of ITO. The bilayer PANI/ITO electrode, therefore, offers special advantages for use in polymer LEDs.

The metallic emeraldine salt form of PANI is prepared by doping and complexation with functionalized sulfonic acids (e.g. camphor sulphonic acid, CSA), yielding a conducting PANI-complex soluble in common organic solvents.[11,12] Thus, PANI-CSA can be spin cast from solution onto substrates such as glass or poly(ethylene terephthalate) to make transparent electrodes.[9,11] The thin PANI-CSA films used in this study were spin-cast from solution in meta-cresol (3.5% by weight) at 8000 rpm and subsequently dried in air at 50°C for 12 hours. The typical thickness of the PANI layers was 600-800Å. Other, thicker PANI layers were also used to compare device performance. The details of device preparation can be found in Ref. 13.

RESULTS AND DISCUSSIONS

Two types of device were fabricated for these studies, one carrier (hole-only) devices and two carrier devices. Since the large work function of copper (4.7eV) reduces the number of electrons injected into the LUMO of MEH-PPV (FIGURE 1 inset), "hole-only" devices fabricated using copper as the cathode allowed the determination of the barrier height at the PANI/MEH-PPV interface.

The barrier heights at the ITO/MEH-PPV and PANI/MEH-PPV contacts were estimated using Fowler-Nordheim field-emission tunneling theory:[14,15]

$$I \propto F^2 \exp\left(\frac{-\kappa}{F}\right) \quad \text{and} \quad \kappa = \frac{8\pi\sqrt{2m^*}\varphi^{3/2}}{3qh}$$

where I is the current, F is the electric-field strength, ϕ is the barrier height and κ is a parameter that depends on the shape of the barrier at the metal-polymer contact. We have assumed that the electric field is constant across the device and that the effective mass equals the free electron mass, thought to be reasonably accurate from self-consistent experiments which are in agreement with predictions for MEH-PPV devices with electrodes having a wide range of work functions.[10]

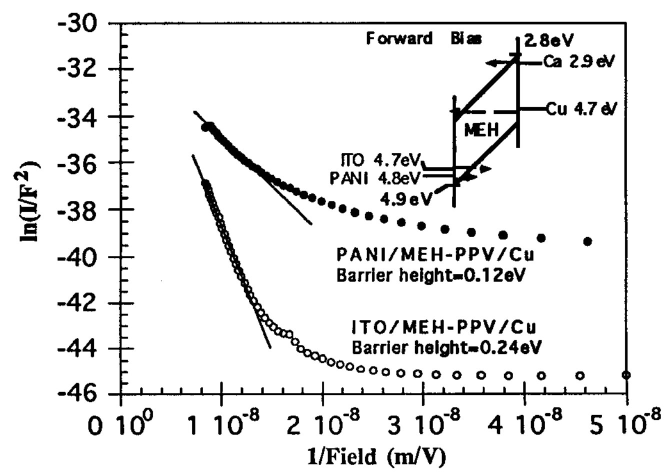

FIGURE 1 Fowler-Nordheim plots for ITO/MEH-PPV/Cu and ITO/PANI/MEH-PPV/Cu single carrier ("hole-only") devices; the inset shows a schematic diagram ofthe energy band diagram in forward bias, indicating the position of the Fermi-level for various electrode materials.

FIGURE 1 shows a plot of $\ln(I/F^2)$ vs. $1/F$ for an ITO/MEH-PPV/Cu device and a PANI/MEH-PPV/Cu device both fabricated with a 1400Å thick MEH-PPV layer. As predicted, the plot is linear at high fields. i.e. above the operating-voltage threshold. The deviation form linearity at lower fields is partly due to bulk conduction through the polymer which, at low fields, is comparable to or greater than the tunneling contribution. In the linear region, the calculated barrier heights for hole tunneling into the devices are 0.2-0.24eV for the ITO/MEH-PPV contact, and 0.08-0.12eV for the PANI/MEH-PPV contact. The barrier height at the Ca/MEH-PPV interface had been estimated from measurements of an "electron-only" device, giving a value of ~ 0.1eV.[10] The band diagram for an LED under forward bias is shown in the inset to FIGURE 1. FIGURE 2 shows the current-voltage (I-V) curves obtained from MEH-PPV LEDs using ITO or ITO/PANI as anode, and using Ca as the cathode material. The device operating voltage of the MEH-PPV LED with an ITO/PANI anode is significantly lower (typically ~ 30-50% lower). In addition, the external quantum efficiency of MEH-PPV LEDs with ITO/PANI anode are about 40~ 50% higher than that of the ITO/MEH-PPV/Ca devices (0.3-0.35% with this specific batch of MEH-PPV).

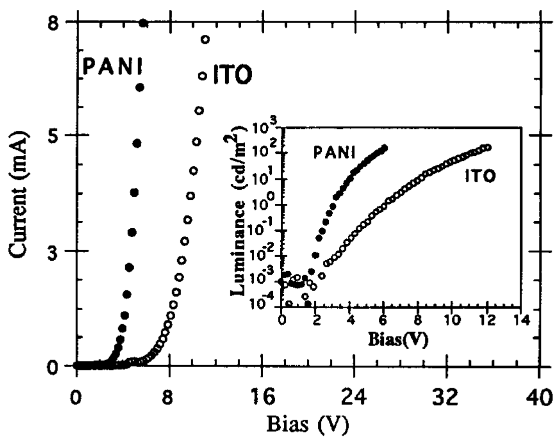

FIGURE 2 I-V characteristics for ITO/MEH-PPV/Ca and ITO/PANI/MEH-PPV/Ca devices. The thickness of the polymer film is about 1300Å; the inset shows the semi-log plot of L-V characteristics for the same devices.

The light vs voltage (L-V) curves always follow the I-V curves. The inset to FIGURE 2 shows a semi-log plot of the L-V curves for the two devices. Both begin to emit light below 2V; however, devices with holes injected through the ITO/PANI electrode into the polymer are much more efficient than devices fabricated with the ITO electrode alone. A calculation of the Fowler-Nordheim tunneling current with different barrier heights shows that this behavior is consistent with the lower barrier height

In order to determine the importance of the ITO layer in the ITO/PANI composite electrode, LEDs with different thickness PANI layers were fabricated without an ITO layer (PANI-only electrodes). It was found that the surface resistance of the PANI electrodes needed to be reduced below 160 ohms/square to reproduce the IV characteristics of the ITO/PANI electrode. Data are shown in FIGURE 3(a) for a PANI(no ITO)/MEH/Ca device. Devices with a PANI layer with surface resistance of ~ 500 ohms/square draw relatively low current during operation, implying that the LED current is limited by the surface resistance of the PANI-only electrode. The resistance of the MEH-PPV layer is R=V/I ~ 1KΩ, comparable to the PANI surface resistance for the 12 mm^2 devices. Using ITO/PANI electrodes, however, the I-V curves are independent of the PANI layer thickness, FIGURE 3(b), indicating that the series resistance of the PANI/ITO bilayer is not limiting. The inset to FIGURE 3(b) demonstrates the excellent transparency of the composite PANI/ITO bilayer electrode; even in the blue portion of the spectrum, the transmittance is about 80%.

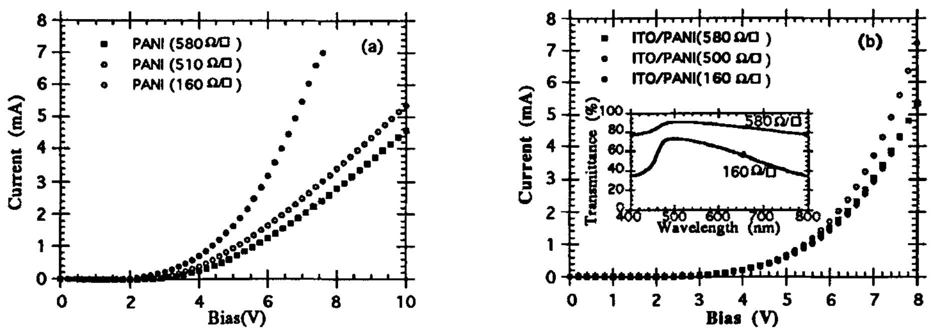

FIGURE 3 (a) I-V characteristics for PANI(no ITO)/MEH-PPV/Ca devices. The thickness of the PANI layer varies from ~ 2500Å (160 Ω/□) to ~ 600Å (580 Ω/□). (b) I-V characteristics for ITO/PANI/MEH-PPV/Ca devices. Inset shows the transmittance of the thin PANI on ITO electrode.

We did not observe any apparent degradation of the MEH-PPV LED due to the PANI electrode. Devices with PANI (or PANI/ITO) anodes show similar IV characteristics after storage in an inert gas environment for more than 6 weeks. Although a small decrease of current was observed, a similar decrease in the injection current was also observed in similar ITO/MEH-PPV/Ca devices. This current decrease might indicate some reaction of Ca with MEH-PPV at polymer-cathode interface.[16] The quantum efficiency also remains constant over the same period of time .

Our experimental results are summarized as follows.

(1) The PANI/ITO electrode has been demonstrated to be an excellent transparent anode for use in polymer LEDs. The PANI/ITO electrode combines the advantages of the higher work function of PANI with the lower surface resistance of ITO.

(2) Using an PANI/ITO electrode, the device operating voltage has been reduced by ~ 30-50%, and the quantum efficiency increased by ~ 30-40%.

(3) The barrier height at the PANI/MEH-PPV interface has been estimated to be 0.08~ 0.12eV.

(4) There is no indication of degradation of the MEH-PPV LED due to the PANI electrode over a period of time of more than six weeks.

We conclude that using PANI-CSA as the anode material improves hole injection into the polymer LED, thereby leading to lower voltage operation and improved efficiency.

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