All-solution processed polymer light-emitting diodes with air stable metal-oxide electrodes

P. de Bruyn,⇑ D.J.D. Moet, P.W.M. Blom

A. Molecular Electronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
B. Dutch Polymer Institute, 5600 AX Eindhoven, The Netherlands
C. Holst Centre, High Tech Campus 31, 5605 KN Eindhoven, The Netherlands

Article info
Article history:
Received 11 October 2011
Received in revised form 6 February 2012
Accepted 11 February 2012
Available online 18 March 2012

Keywords:
Organic
LED
Solution processing
Metal oxide
Air stable

Abstract
We present an all-solution processed polymer light-emitting diode (PLED) using spincoated zinc oxide (ZnO) and vanadium pentoxide (V2O5) as electron and hole injecting contact, respectively. We compare the performance of these devices to the standard PLED design using PEDOT:PSS as anode and Ba/Al as cathode. We show that the all-solution processed PLEDs have an equal performance as compared to the standard design directly after fabrication. However, the ambient stability of the PLEDs with spincoated transition metal oxide electrodes is exceptionally good in comparison to the standard design.

1. Introduction

Polymer light emitting diodes hold the promise of large-area lighting at low cost [1]. However to achieve low costs all material layers in the device, including the injecting contacts, should be deposited from solution to fully benefit from a cheap production method such as roll-to-roll processing. In practice this excludes the use of low work function metal contacts, since they generally have to be evaporated in vacuum and are extremely sensitive to oxygen and moisture. The use of these metals is necessary to ensure efficient electron injection into the lowest unoccupied molecular orbital (LUMO) of the light emitting polymer due to its low electron affinity of typically 2–3 eV. This low electron affinity of light-emitting polymers intrinsically provides a great challenge for the air stability of the electron injecting contact [2]. Transition metal oxides such as zinc oxide (ZnO) and titanium oxide (TiO2) have proven to be promising candidates for overcoming this problem. Specifically, systems with evaporated molybdenum trioxide (MoO3) as hole injecting contact and ZnO or TiO2 as electron injecting contact have been studied extensively [3,4]. The enhanced hole injection properties of MoO3 compared to poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS), especially when injecting into polymers with very deep HOMO levels, has been abundantly proven in literature [5–10]. Furthermore, thermally evaporated vanadium pentoxide (V2O5) has been shown to provide an ohmic injecting contact to luminescent polymers and polymer:fullerene solar cells as well [11–14]. However, a big challenge to overcome is the realization of metal oxide electrodes that are processed from solution, combining efficient charge injection with air stability. A solution-based process to produce amorphous V2O5 has already been developed in the last century [15–17] and has recently been revisited and introduced as anode in organic solar cells by Larsen-Olsen et al. [18].

Here we introduce organic light emitting diodes with ZnO and V2O5 injecting contacts through a fully solution
deposited and low temperature route. ZnO can be created through the spin casting and subsequent decomposition of zinc acetylacetonate ($\text{Zn(acac)}_2$) under ambient conditions and at low temperatures ($130 ^\circ \text{C}$ [19,20]). $\text{V}_2\text{O}_5$ is deposited by diluting vanadium oxytriisopropoxide in isopropanol and spin casting this solution in ambient conditions to yield a layer of $\text{V}_2\text{O}_5$. The procedure to create the $\text{V}_2\text{O}_5$ layer does not require post-processing heat treatment, making the entire process compatible with cheap flexible substrates such as PET. For the emitting polymer, we chose the polyfluorene copolymer poly[9,9-didecane-fluorene-alt-(bis-thienylene)benzothiadiazole] (PF10TBT). An advantage of this red-emitting polymer compared to fluorene-alt-(bis-thienylene)benzothiadiazole] (PF10TBT).

3. Results and discussion

3.1. Evaluation of the spincoated ZnO cathode

In order to evaluate the performance of the spincoated ZnO cathode and $\text{V}_2\text{O}_5$ anode separately we first make use of a test device (Fig. 1). This inverted device contains a spincoated ZnO cathode as bottom contact and an evaporated MoO$_3$/Au hole injecting contact as top contact. This evaporated MoO$_3$/Au anode has been proven to be an Ohmic contact on polyfluorene derivatives with a very deep HOMO level ($-6.0 \text{eV}$ below vacuum). [5] As a result also on the PF10TBT polymer studied here, with the HOMO level at $-5.4 \text{eV}$, we can be sure that this hole contact is ohmic, enabling to investigate the performance of the spincoated ZnO cathode. As a first step the electrical characteristics of the inverted devices with a solution processed ZnO electron injecting bottom contact and an evaporated MoO$_3$/Au hole injecting top contact are compared to conventional devices with a PEDOT:PSS and Ba/Al contact for hole and electron injection, respectively. Fig. 2 shows the current density–voltage ($J–V$) and light–output–voltage ($L–V$) characteristics (Fig. 2a), as well as the ratio of the light output and the current as a function of voltage (Fig. 2b), which is a measure for the PLED efficiency. The inset of Fig. 2b shows the current of the devices on a double log scale.

First of all, what can be discerned is close congruence between the efficiencies of the two architectures. This is a strong indication that the electron injection is efficient and that the ZnO forms an ohmic electron contact on PF10TBT. This is further confirmed by the fact that after correction for the built-in voltage the current densities of the conventional and inverted devices are equal and, as shown in the inset of Fig. 2b, follow a space-charge limited trend, suggesting ohmic injecting contacts in both cases.

For a PLED with Ohmic contacts the current density in the plasma limit is given by [21]:

$$J = \left(\frac{9\pi}{8}\right)^{1/2} \varepsilon_0 \varepsilon \left(\frac{2q\mu_H \mu_n (\mu_p + \mu_n)}{\varepsilon_0 e_B} \right)^{1/2} \frac{(V - V_{bi})^2}{L}$$

$$= \frac{9}{8} \varepsilon_0 \varepsilon \mu_{eff} \left(\frac{V - V_{bi}}{L}\right)^2,$$  \hspace{1cm} (1)

with $J$ the current density, $\varepsilon_0$ the permittivity of vacuum, $\varepsilon$ the relative dielectric constant of the polymer, $\mu_p$ and $\mu_n$ the hole and electron mobility, $B$ the bimolecular recomb-
nation constant, $V$ the applied voltage and $L$ the thickness of the polymer layer. Taking $\varepsilon = 3$ and $L = 80$ nm, the effective mobility $\mu_{\text{eff}}$ derived in this fashion amounts to $6.0 \times 10^{-9}$ m$^2$/Vs, in agreement with previous determinations [22]. Furthermore, a decrease in the turn-on voltage is observed, as previous publications have shown as well [3]. The exact origin of the decrease in the turn-on voltage is still under investigation. In the standard metal–insulator–metal model it would imply a decrease in the difference between the work functions the contacts in these devices. In that case small contact barriers would be present in the device. The current–voltage and efficiency–voltage characteristics, however, show an efficient charge injection for this specific combination of light-emitting polymer and contacts. In a recent study (M. Lu et al. submitted to JAP) we found that holes injected from the anode get trapped at the ZnO/semiconductor interface. The resulting electric field enhances the injection of electrons from the ZnO in the polymer, explaining the good efficiencies. Next we consider the ambient stability of these devices under two conditions, (a) storage in air and (b) operation in air. Fig. 3a and b shows the pristine and the $J$–$V$ characteristics after 24 h of storage in air of the conventional and inverted devices, respectively. The normal geometry device has lost most of its functionality after 24 h of storage in air, while the inverted geometry device remains intact. Besides the
storage stability, also the operational stability is essential. Fig. 4a and b shows the $J$–$V$ curves for pristine devices and after operation in air for 24 h at $10^3$ A/m$^2$ for conventional and inverted geometry LEDs, respectively. The conventional device degrades rapidly in air as a consequence of the deteriorating properties of the electron injecting Ba contact upon exposure to air. After 24 h the conventional device has ceased functioning. This degradation is related to rapid degradation of the barium contact layer. After deposition a BaAl$_4$ alloy is formed at the interface with the polymer [23]. Upon exposure to water that penetrates through the pinholes in the Al cover layer an insulating Al(OH)$_3$ layer is formed at the interface. This layer effectively prevents electron injection and therefore kills the electroluminescence, leading to the formation of black spots. The inverted device however maintains a high current density and light output. Since the emitting polymer layer is identical in both cases, the only conclusion is that
the differences in degradation behavior are caused by the difference in contacts. Therefore the metal oxide contacts show excellent ambient stability in injecting charges, compared to the conventional contacts. Besides this quantitative difference, Fig. 5 also shows the deterioration qualitatively. Depicted are photographs of the devices operating in ambient conditions after set periods of time. Both devices were consistently captured in a single frame for equal lighting conditions, as well as being operated at the same initial current density of $10^3 \text{ A/m}^2$. The formation of dark areas of zero electroluminescence can clearly be seen in the conventional device, starting mere minutes after exposure to air, eventually breaking down completely after approximately 19 h. The distinctive nucleation of these spots and their growth can evidently be seen on the photographs. In contrast, the inverted geometry device remains uniform, in agreement with the results obtained from the electrical measurements. We can therefore conclude that the spin-
coated ZnO bottom cathode injects electrons efficiently into PF10TBT and also exhibits excellent air stability as compared to the commonly used thermally evaporated low work function metal electrodes.

3.2. Evaluation of the solution processed V$_2$O$_5$ anode

Finally we compare the characteristics of the fully solution processed system with a spincoated V$_2$O$_5$ anode to the
reference device with the evaporated MoO3 anode. Fig. 6a
shows a comparison of the J–V characteristics of the two
devices, as well as the J–V curves of the V2O5 based LED
in its pristine state and after operation in air for approxi-
mately 92 h in Fig. 6b. The performance of the two systems
is remarkably similar. The current density is even slightly
higher for the solution processed V2O5 device, due to a
slightly thinner polymer layer. The electrical characteriza-
tion clearly shows that both materials give an ohmic hole
injecting contact to the polymer highest occupied molecu-
lar orbital (HOMO). Similar stability to the evaporated
MoO3 LED can be observed in the V2O5 devices, showing
only little degradation after 92 h of operation in ambient
conditions, further exemplifying the excellent air stability
of metal oxide materials. As a result an all-solution pro-
cessed PLED with two ohmic contacts has been realized.
The fact that these PLEDs are also stable in air for various
hours without encapsulation is beneficial for a roll-to roll
production process. It implies that the PLEDs can first be
processed roll-to-roll from solution and that later on a bar-
rier foil can be laminated to the device. Another intriguing
question is what kind of requirements with regard to the
water vapor transmission rate of the barrier stack are
needed for this type of all-solution processed PLEDs, which
is a subject of further research.

3.3. Characterization of the spincoated ZnO cathode

To address the chemical properties of the spin cast ZnO
layer, Fourier transform infrared spectroscopy (FTIR) mea-
surements were performed on these films. Fig. 7 shows the
mid-infrared spectrum of a film of the Zn(acac)2 precursor
and a typical ZnO film. Several features can be distin-
guished. The vibrations of Zn(acac)2 around 3000–
3400 cm\(^{-1}\) and in the range 400–1600 cm\(^{-1}\) are well docu-
mented and correlate to the peak positions found here
[24]. After conversion to ZnO we see a clear peak appearing
at 418 cm\(^{-1}\), that originates from the Zn–O vibration peak,
demonstrating that indeed ZnO has formed. Furthermore,
additional features in the ZnO spectrum appear between
800 and 1600 cm\(^{-1}\). These features can be identified as a
hydrozincite species, which can easily form on ZnO under
ambient conditions, as described in literature [25]. From
the good performance of both solar cells (Ref. [19]) and
PLEDs presented here with this precursor ZnO we can con-
clude that the hydrozincite species does not hinder the
electrical properties.

4. Conclusions

An all-solution processed PLED has been realized with
spin coated metal oxide contacts. The performance of these
PLEDs is equivalent to the performance of conventional
PLEDs with a PEDOT:PSS anode and a thermally evaporated
low work function metal electron injecting contact. The
ambient stability of the all-solution processed PLEDs is
greatly enhanced as compared to the devices with the con-
ventional architecture. The results presented here promise
a low cost, universal and facile solution based production
process for PLEDs using air stable metal oxide contacts.

Acknowledgements

The authors would like to acknowledge the Dutch Poly-
mer Institute for funding through DPI Project #660. Fur-
thermore the authors are grateful for technical support of
J. Harkema and F. van der Horst.
References