Available online at www.sciencedirect.com
SCIENCE DIRECT®

Synthetic Metals 147 (2004) 155–158

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Polymer light-emitting diodes with spin-polarised charge injection

A. Hayer[a,*], A. Köhler[a], E. Arisi[b], I. Bergenti[b], A. Dediu[b], C. Taliani[b],
M. Al-Suti[c], M.S. Khan[c]

[a] *Cavendish Laboratory, University of Cambridge, UK*
[b] *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Bologna, Italy*
[c] *Department of Chemistry, Sultan Qaboos University, Oman*

Received 8 June 2004; received in revised form 10 June 2004; accepted 10 June 2004
Available online 22 October 2004

Abstract

This study is concerned with the characterisation of the injection properties of the manganite compound $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and its use as a spin-polarised anode in polymer light-emitting diodes. Charge carrier injection and electroluminescence in a polymer LED with an LSMO anode is achieved. A dependence of the current–voltage characteristics of LEDs with LSMO anodes on the temperature is observed and compared to the behaviour of LEDs with standard ITO anodes. The temperature dependence is shown to be due to improved hole injection at low temperatures, possibly originating from magnetic ordering upon cooling.

Keywords: Polymer light-emitting diodes; Spin-polarised charge injection; Spintronics

1. Introduction

The efficiency of polymer light-emitting diodes used for display applications depends crucially on the ratio of emissive singlet excitons to non-emissive triplet excitons formed upon charge carrier recombination in the device. The spin of the exciton is determined by the overall spin of the electron–hole pair it is formed from. In the case of spin-independent charge carrier injection and spin-independent recombination to the exciton state, it follows from spin statistics that only 25% of the excitons will be singlets. In conventional organic materials, radiative decay from the triplet state to the (singlet) ground state is spin-forbidden so that only singlet excitons will return to the ground state via light emission. Thus, LED efficiency is strongly influenced by the generation ratio of singlet to triplet excitons.

One approach to influence this ratio is to inject only spin-up or only spin-down charge carriers into the organic semiconductor. Such a spin-polarised charge carrier injection can be achieved by employing electrode materials that are magnetic at room temperature. The suitability of the manganite compound $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) as a semi-transparent anode with a Curie temperature of 350–370 K has previously been demonstrated for small molecule LEDs [1]. Recent magnetoresistance measurements confirm that the injection from LSMO into organic semiconductors is in fact spin-polarised [2] and that giant magnetoresistance can be achieved [3].

Here we look at the suitability of LSMO as an anode in LEDs with conjugated polymers as semiconductors. Conjugated polymers and monomers that show both singlet and triplet emission have been used to directly determine the singlet generation fraction in working LEDs [4]. Their radiative triplet emission becomes partially allowed through enhanced spin–orbit coupling due to the inclusion of heavy Pt atoms in the conjugated backbone. However, those materials have to be deposited via spin-coating as they are not stable to evaporation, the method used for the fabrication of small molecule LEDs. The effect of spin-polarised charge carrier injection on the singlet exciton generation fraction could then be de-

---

* Corresponding author.
E-mail address: ah385@cam.ac.uk (A. Hayer).

0379-6779/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2004.06.031

termined using the method cited above [4]. In this method, the singlet generation fraction is determined from the different spectral weight that phosphorescence has with respect to fluorescence in photoluminescence as compared to electroluminescence. While in photoluminescence, all excitons are initially created as singlets, in electroluminescence, fractions χ_S and χ_T are created as singlets and triplets, respectively. Thus, comparing electroluminescence to photoluminescence yields the singlet generation fraction.

The present study shows the preparation of spin-coated polymer LEDs on semitransparent spin-polarised LSMO anodes. Electroluminescence and temperature-dependent injection characteristics are studied.

2. Experimental

The preparation of thin LSMO films on $SrTiO_3$ substrates [1] and the synthesis of the Pt-quinoxaline polymer P42 [5] used in this study are described elsewhere. F8BT and TFB were obtained from Dow Chemical Company through CDT Ltd. The chemical structures of the polymers used in this study are shown in Fig. 1. Single-layer LEDs are prepared by spin-coating a polymer solution onto either as-prepared LSMO substrates or ITO substrates and subsequently evaporating cathodes consisting of 20 nm of Ca capped with 120 nm of Al.

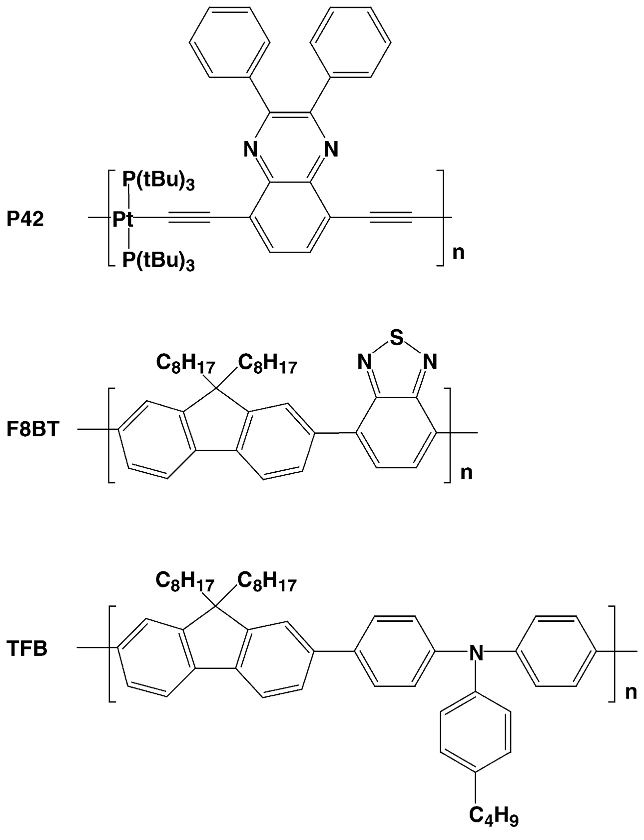

Fig. 1. Chemical structure of the polymers used.

Measurements are carried out with the sample under vacuum in a continuous flow helium cryostat. Current–voltage characteristics are obtained using a Keithley 2400 SourceMeter. Electroluminescence spectra are recorded using a spectrograph with an optical fibre input coupled to a cooled CCD detector (Oriel InstaSpec IV).

3. Results and discussion

At room temperature, the currents injected into an LED composed of an LSMO anode and the Pt-quinoxaline polymer P42 proved to be too low to generate electroluminescence. As P42 shows electroluminescence on ITO, this points towards a problem with the hole injection from LSMO into P42. In order to clarify this, the temperature-dependent injection properties of both ITO and LSMO were studied. Current–voltage characteristics of LEDs with P42 on ITO and on LSMO at different temperatures are compared in Fig. 2. For ITO anodes, injected currents decrease as the temperature decreases. This behaviour is expected as charge transport in a disordered organic semiconductor occurs via a thermally activated hopping transport and is thus slowed down at lower temperatures. For LSMO anodes, on the other hand, currents in forward direction increase with decreasing temperature

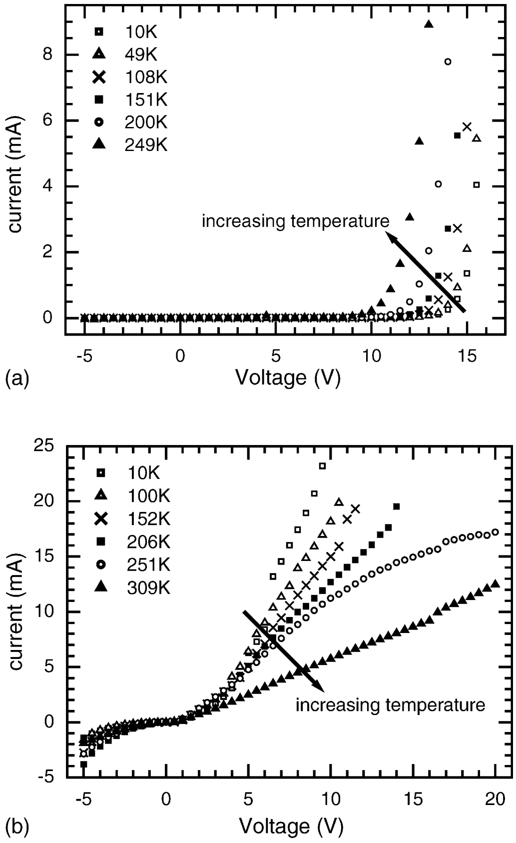

Fig. 2. Current–voltage characteristics of an LED of the structure ITO/P42/Ca/Al (a) and of the structure LSMO/P42/Ca/Al (b) with varying temperature.

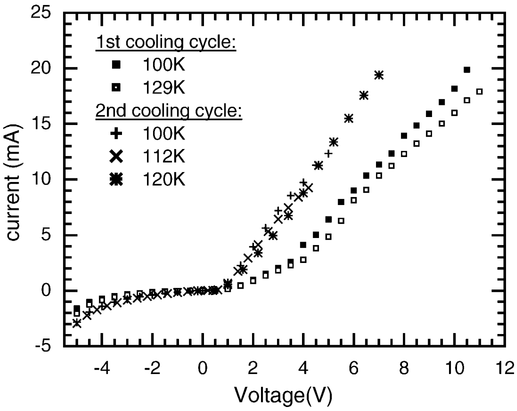

Fig. 3. Current–voltage characteristics of an LED of the structure LSMO/P42/Ca/Al in two subsequent cooling cycles.

and the rectification ratio is enhanced. This cannot be due to a change of the charge carrier transport in the semiconductor as the polymer is identical in both devices studied. We subsequently tested a range of purely organic polymers as emissive layers on LSMO and found that indeed, the same behaviour occurs. In addition, we observed a hysteresis upon re-heating the device; the currents do not fall back to values as low as those obtained when starting the measurement at room temperature. Furthermore, as shown in Fig. 3, if the device is subjected to a second cooling cycle, currents at any given temperature are higher than those observed at the same temperature in the first cooling cycle.

We consider that magnetic ordering upon cooling might be a possible explanation for such a behaviour. LSMO has a ferromagnetic metallic and a paramagnetic insulating phase. In the bulk, it is ferromagnetic metallic at room temperature. A hypothesis is that in thin films, paramagnetic metallic inclusions can reduce both the conductivity and the ability to inject holes into the organic semiconductor. The spins in these domains can then be aligned upon lowering the temperature. This ordering will only partially be lost upon reheating. This would explain both the hysteresis upon reheating and the higher currents in a second cooling cycle. Similarly, another hypothesis would be that CO, CO_2 and hydrocarbon impurities adsorbed on the LSMO surface [6] lead to a magnetic disorder of the corresponding Mn sites that can be broken by lowering the temperature. In any case, the observed temperature-dependent current–voltage characteristics can only be explained through an improved charge carrier injection at low temperatures.

At 10 K, currents in LEDs with P42 on LSMO anodes are higher than those previously needed to achieve emission from an LED of P42 on ITO. Yet, electroluminescence from P42 on LSMO could not be obtained. This points towards charge carrier imbalance. If the high currents observed originate almost exclusively from one type of charge carriers, most of these will not find a partner to recombine with and thus will not emit light. To address this problem, a blend of the hole transporting host polymer TFB and the efficient singlet emitting polymer F8BT was used in an LED with an LSMO anode. The energy levels of these materials (Fig. 4) correspond very closely to those of TPD and Alq_3 used in a small molecule device that was previously shown to give electroluminescence on LSMO [1]. Particularly, the use of TFB should improve hole injection. As shown in Fig. 5, electroluminescence could in fact be observed from F8BT:TFB on LSMO. The electroluminescence spectrum exactly matches the spectrum of F8BT:TFB on ITO.

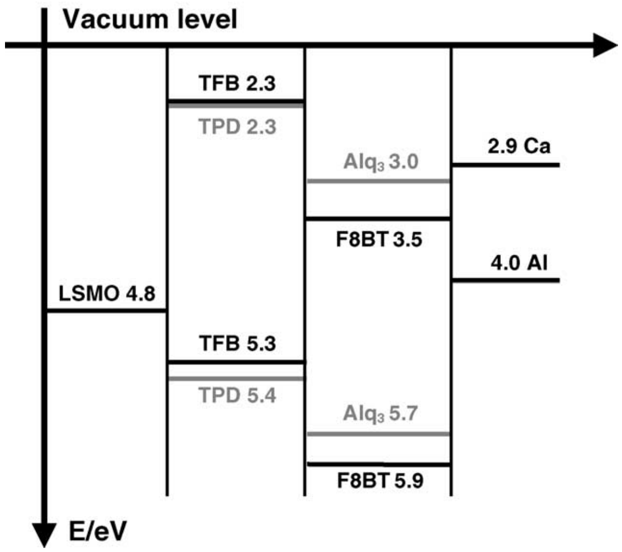

Fig. 4. Energy level diagram of the materials used in the polymer and in the small molecule approach.

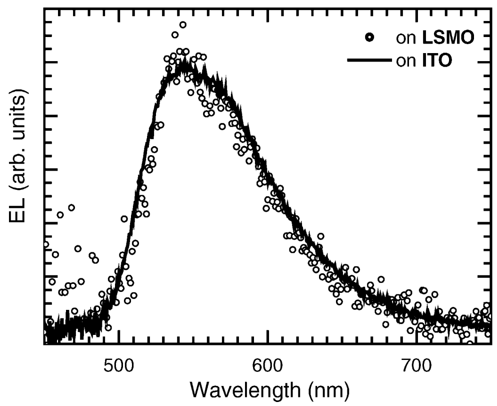

Fig. 5. Electroluminescence spectra of F8BT:TFB on LSMO and on ITO anodes.

4. Conclusions and further work

Polymer electroluminescence from an LED containing the spin-polarised anode $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) has been achieved using the hole transporting polymer TFB as a host for the efficient singlet emitting polymer F8BT. In a next step, this can be extended to including a polymer emitter that shows both singlet and triplet emission. Thus the fraction of electron–hole pairs recombining to form a singlet exciton and the influence of spin-polarised charge carrier injection on this fraction will be accessible to experiment.

The temperature-dependent injection characteristics of LSMO are studied. Improved injection into organic semiconductors at low temperatures is shown. This can possibly be attributed to a magnetic ordering of the anode upon cooling. Further work will focus on surface treatment such as vacuum annealing or surface etching before polymer spin-coating to determine whether this ordering is intrinsic to LSMO, involving paramagnetic insulating inclusions in thin LSMO films, or whether it occurs in CO, CO_2 and hydrocarbon adsorptions on the LSMO surface.

References

[1] E. Arisi, I. Bergenti, V. Dediu, M.A. Loi, M. Muccini, M. Murgia, G. Ruani, C. Taliani, R. Zamboni, J. Appl. Phys. 93 (2003) 7682.
[2] V. Dediu, M. Murgia, F.C. Matacotta, C. Taliani, S. Barbanera, Solid State Commun. 122 (2002) 181.
[3] Z.H. Xiong, D. Wu, Z.V. Vardeny, J. Shi, Nature 427 (2004) 821.
[4] J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, M.S. Khan, A. Köhler, R.H. Friend, Nature 413 (2001) 828.
[5] J.S. Wilson, A. Köhler, R.H. Friend, M.K. Al-Suti, M.R.H. Al-Mandhary, M.S. Khan, P.R. Raithby, J. Chem. Phys. 113 (2000) 7627.
[6] M.P. de Jong, V.A. Dediu, C. Taliani, W.R. Salaneck, J. Appl. Phys. 94 (2003) 7292.