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Electroluminescence and electrical properties of White-OLEDs studied by dc and ac measurements

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Abstract

White-OLEDs were made by thermal evaporation using NPB (N, N'-Bis (naphthalen-1-yl)-N, N'-bis (phenyl) benzidine) doped with DCM1 (4 - (Dicyanomethylene) – 2 – methyl – 6 - (4 -dimethylaminostyryl)-4H-pyran) in a single layer with two emitters. The electroluminescent emission has a CIE (x, y) color coordinates of (0.32, 0.37) with a brightness around 350 cd/m^2 and a maximum luminous efficiency of 0.5 cd / A in normal view direction. Under dc conditions the electroluminescence changes almost linearly with the applied voltage with no noticeable change in color coordinates. The ac electrical measurements show the relaxation frequencies in order of a hundred of kH and can be correlated with the parallel RC models associated to the emissive organic layer. The simulated electrical behavior shows a good balanced contribution for the two active layer emitters..

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Keywords: White-OLED; Electroluminescence; Electrical properties; doping

1. Introduction

The developments of Organic Light Emitting Diodes (OLEDs) since the first multilayered device [1] induces to a high intense research looking for many technological applications. Perhaps one of the most studied applications in recent years after the display, is the solid state lighting including not only decorative but also general light. In the last case, the white-OLEDs (WOLEDs) is a recurrent topic that involving a noticeable investigation.

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Many approaches have been used to produce a WOLED suitable for lighting [2 – 4]. The conventional RGB stacked emitter (white color achieved with a mix of these colors) was extensively studied but besides its success, the structure complexity turns the final device difficult to reproduce and is almost incompatible with large scale production. The attempt to obtain a simple WOLED emitter was produces interesting results but they show some problems related with the efficiency, reproducibility and color changes with driving current. Although with some questions to overcome, the simple WOLED structure containing two primary colors emitters as found to be the most interesting for future applications [5 – 10]. Typically, such structures involve either two light emitting layers or a single layer with two emitters embedded, in a directly stacked layer. For the emitting colors, the blue and red (or orange-red, typically a dye) has been used. Such kind of structures offers practical advantages, like simplicity, efficiency, low cost and fabrication effectiveness. However, the two different color emitters can compete together upon electrical field application and the overall color performance can vary; and for some dyes and specific layer doping, the charge-induced fluorescence quenching reduces the efficiency. For this last question, the design of new materials and the mix layers composition, are the actual pathway; for the other question, the problem can be suppressed by the introduction of electron and / or hole blocking layers. Besides such questions, it is also important to analyze the electrical properties of such direct stack layers in order to understand how each material with own electrical properties can influence the overall behavior. The small signal analysis is a suitable tool for that [11 – 13].

This study describes the properties of a WOLED with a direct stack emitting layer comprises by a blue and an orange-red emissive materials. The simple structure, with a hole blocking layer, appears to be very stable with no noticeable changes in the CIE color coordinates upon applied voltage changes. The effects on the electrical behavior of an emissive layer composed by two distinct emitter was analyzed by small signal spectroscopy. The result reveals that the emissive layer can be considered as composed by only one material.

2. Experimental

The WOLEDs was made by thermal evaporation on glass substrates. The organic materials used was the NPB (N, N'-Bis (naphthalen-1-yl)-N, N'-bis (phenyl) benzidine) as hole transport layer, and Alq3 (tris (8-hydroxyquinoline) aluminum) as electron transport layer. BCP (3-Benzidino-6-(4-chlorophenyl) Pyridazine) and DCM1 (4 - (dicyanomethylene) – 2 – methyl – 6 - (4 -dimethylaminostyryl)-4H-pyran) were used as the hole blocking layer and hole transport layer dopant respectively. The ITO (indium tin oxide) as used as transparent anode and aluminum was used as cathode. The final structure was ITO / NPB: 1% (in mass) DCM1 (40nm) / BCP (10nm) / Alq3 (30nm) / Al. The evaporation rate was about 3 Å/s for all layers. The device area is 25 mm^2. Figure 1 shows the general device scheme as well the organic molecular structures of the materials used.

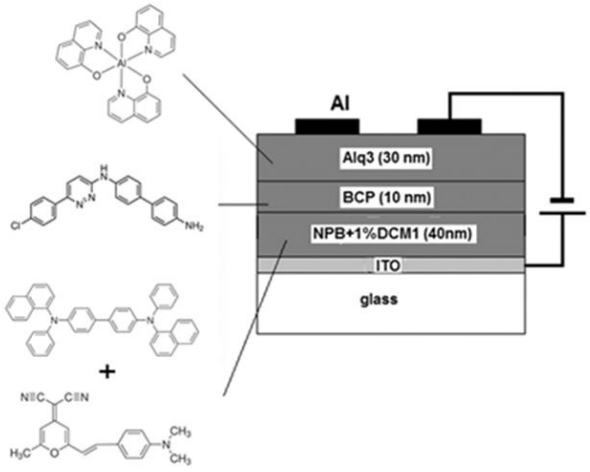

Fig. 1. WOLED general scheme and molecular structures of the materials used.

The electrical characterization was performed with a 2420 Keitley Voltage Source Meter (dc) and an RLC Meter Fluke PM6306 (ac), the emission spectra were obtained with an OcenOptics USB400 Spectrometer and the brightness was measured with a Minolta LS100 luminance meter.

3. Results and Discussion

In figure 2a a WOLED electroluminescence spectrum (DCM1) is shown for an applied voltage of 18 V. In the inset, a photograph of a device and the CIE color coordinates diagram are shown.

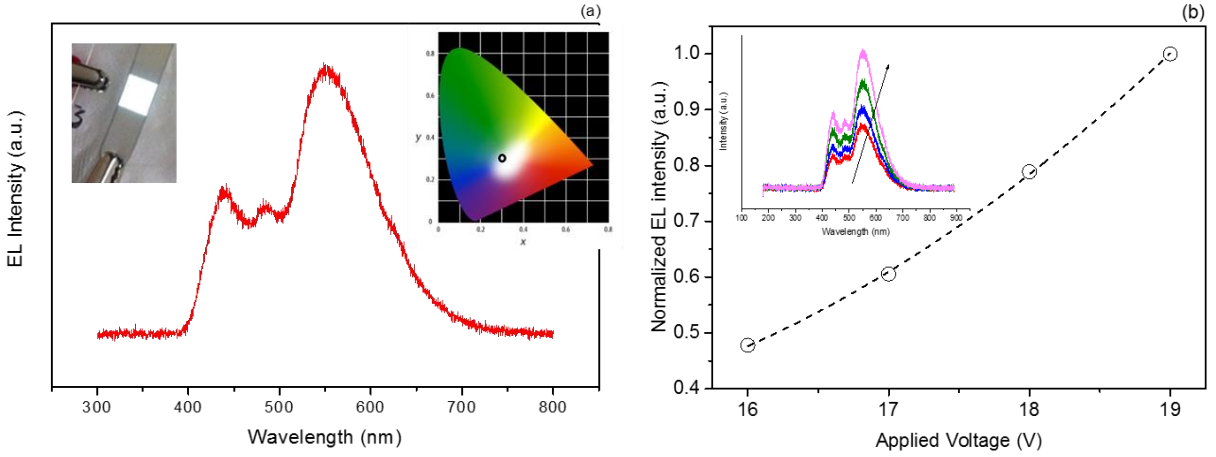

Fig. 2. a) Electroluminescence spectra for an applied voltage of 18V. Inset: the CIE coordinates and the WOLED photograph. b) Normalized electroluminescence with applied voltage. The arrow shows the increase of the applied voltage.

The observed emission is dominated by the blue spectrum (NPB) and the orange-red emission (DCM1). The result is the sum of such complementary colors giving an emission near the pure white (0.32, 0.37). Several experiments was made changing the dopant concentration from 0.5 to 2 %. The effective best results was obtained with the doping concentration of 1%; bellow such value, there is a noticeable change of the color coordinates towards the blue region (from the NPB emission) while for higher values, the CIE coordinates approach to the yellow spectral region due to the high DCM1 emission band. As a small change in DCM1 concentration changes significantly the color coordinates, a fine tune remains opened. Changing the applied voltage, no major differences was observed in the color coordinates; only the overall electroluminescence band intensity changes, accordingly the voltage value, keeping the relative intensity of the blue and orange bands quite constant. The results for several applied voltages can be viewed in figure 2b. The electroluminescence intensity for different applied voltages can be fitted to a simple polynomial trend but quite linear, as similar to the observed for the organic emitters alone. This is an important result, indicating that in such active layer the two emitters have its own recombination and emission process and don't compete, resembling a cooperative emission.

The WOLED current-voltage-bright (I-V-L) behavior is shown in figure 3, also for an active layer of 1% of DCM1. The driving voltage (around 12 V for all samples with 40 nm active layer thickness) is directly correlated with the transition from a relatively ohmic to a space charge limited current region. The typical maximum stable bright (only measured perpendicularly to the emitting area) is about 350 cd/m2 giving a maximum efficiency of 0.5 cd/A (in same conditions). Considering only the normal view direction, this is a relatively good result. Moreover, in the dynamic voltage range (from 12 to 20 V) the output, besides the almost linearity, is very stable and reversible.

Although a relative high driving voltage, the electrical current is relatively low, giving a medium power consummation device.

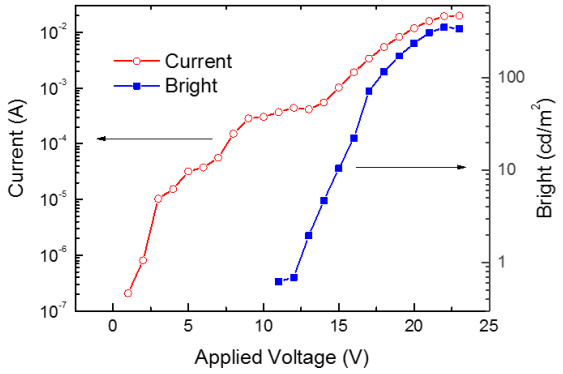

Fig. 3. The electrical current – luminance vs applied voltage for a WOLED with a 40 nm active layer thickness. The bright is taken under normal view incidence.

An attempt to tuning the CIE color coordinates by changing also the active layer thickness shown that no appreciable changes was obtained for thickness ranging from 30 to 50 nm. Bellow 30 nm the device becomes unstable and above 50 nm a relative high resistance is found, increasing the driving voltage, lowering the efficiency and increasing the probability of disruption. Although no changes in color coordinates (similar spectra shapes), the 40 nm tick active layer is the best compromise between the I-V-L data (and therefore the efficiency) although a low driving voltage can be found for the 30 nm tick active layer as expected.

Impedance spectroscopy (small signal analysis) is an important tool for device characterization. Using such technique, it is possible to establish an equivalent circuit that can sometimes be correlated with the fundamental device electrical properties. In order to get insight about the electrical nature of the NPB:DCM1 active layer, devices with structure of ITO / NPB: 1% DCM1 (40nm) / Al was made. The capacitance (C) and conductance over frequency (loss - G / ω) are shown in figure 4a. Figure 4b shows the Cole-Cole plot for the same C and G / ω.

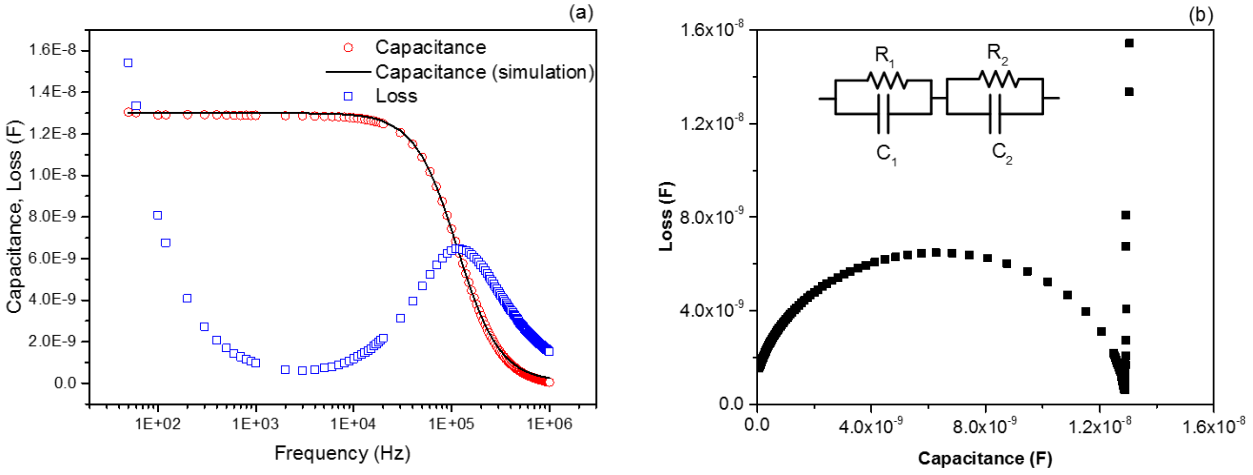

Fig. 4. (color online) a) capacitance (o) and loss (□) for a device of ITO / NPB: 1% DCM1 (40 nm) / Al. Bias of 0 V. b) Cole-Cole plot. Inset: the equivalent circuit used.

Several equivalents electrical circuits can be adjusted to the experimental data 14 each of them corresponding to a specific physical meaning. For the general behavior found, data can be adjusted to an equivalent circuit that is shown in the inset of figure 4b. Such equivalent circuit is generally attributed to a device that haves two major contributions to the ac signal, one arising from an electrical barrier (the first RC circuit and in our case the cathode electrode) and a second arising from the semiconductor bulk (the second RC circuit). The Cole-Cole plot is characteristic. A simulation of such general electrical circuit is observed by the full line in figure 4a for the capacitance data. The best numerical results gives $R_1 \sim 20$ k Ω, $C_1 \sim 10$ nF, $R_2 \sim 500$ Ω and $C_2 \sim 0.1$ nF. These data are compatible with a barrier interface (RC circuit 1) and a semiconductor bulk (RC circuit 2). Others fits, in particular the simple RC model or two parallel RC can be tested. Whit our work, we cannot fit the experimental data with such models. Sometimes is used a model comprising a constant phase element 11 instead a fixed capacitor, in order to accommodate several physical questions like spatial inhomogeneities and dopant effects. Although possible (and perhaps important in our active layer blend), the fitted data to such model leads to a constant capacitor. The result is particular interesting as shows a good uniformity of the active layer resulting from the co-evaporation of two different materials. This is important for the device usefulness indicating that the two emitters acts independently but with an overall result that seems equivalent to one only material layer.

The overall results shows a very stable basic and simple structure for a WOLED development, without the common problems arising from a directly stacked active layer. Further improvements can be made, in particular to reduce the driving voltage and increases the current efficiency.

4. Conclusions

WOLEDs was successfully fabricated in a simple device structure using a directly stacked active layer formed by a blue emitter (NPB) doped with an orange-red emitter (DCM1), based on the two complementary colors principle. The optimal doped concentration for white emission is 1% in mass, giving CIE color coordinates of (0.32, 0.37). A best compromised layer thickness is of 40 nm, leading to a maximum stabilized bright of 350 cd/m^2 and a luminous efficiency of 0.5 cd / A, both only in a normal view direction. Small signal analysis shows that electrical response of such active layer can be given by two RC circuits interpreted in terms of an electrode barrier and only one material active layer. This result is compatible with a cooperative emission. Whit these overall data, further developments are possible.

Acknowledgements

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References

[1] C.W. Tang and S.A. VanSlyke, Appl. Phys. Lett., 51 (1987) 913
[2] Young Wook Ko, Choong-Heui Chung, Jin Ho Lee, Yong-Hae Kim, Choong-Yong Sohn, Bong-Chul Kim, Chi-Sun Hwang, Yoon-Ho Song, Jongtae Lim, Young-Joo Ahn, Gi-Wook Kang, Namheon Lee and Changhee Lee, Thin Solid Films, 426 (2003) 246
[3] Yao-Shan Wu, Shiao-Wen Hwang, Hsian-Hung Chen, Meng-Ting Lee, Wen-Jian Shen and Chin H. Chen, Thin Solid Films, 488 (2005) 265
[4] Wenbin Chen, Lili Lu and Jianbo Cheng, Optik, 121 (2010) 107
[5] CH. Chuen and Y.T. Tao, Appl. Phys. Lett., 81 (2002) 4499
[6] K.O. Cheon and J. Shinara, Appl. Phys. Lett., 81 (2002) 1738
[7] When-Chan Sheen, Y.K. Su and Liang-Wen Ji, Materials Science and Engineering A, 445-446 (2007) 509
[8] Tianle Li, Wenlian Li, Xiao Li, Liangliang Han, Bei Chu, Mingtao Li, Zhizhi Hu and Zhiquiang Zhang, Solid-State Electronics, 53 (2009) 120
[9] Chih-Hung Hsiao, Yi-Hsin Lan, Pei-Yu Lee, Tien-Lung Chiu and Jiun-Haw Lee, Org. Electronics, 12 (2011) 547
[10] Chuang-Cheng Tsou, Huei-Tzong Lu and Meiso Yokoyama, J. Crystal Growth, 280 (2005) 201

[11] Ching-Chia Chen, Bo-Chao Huang, Ming-Shiang Lin, Yin-Jui Lu, Ting-Yi Cho, Chih-Hao Chang, Kun-Cheng Tien, Su-Hao Liu, Tung-Hui Ke and Chung-Chih Wu, Org. Electronics, 11 (2010) 1901
[12] Shingo Ishihara, Hiroyuki Hase, Takayuki Okachi and Hiroyoshi Naito, Phys. Status Solidi C, 12 (2012) 2561
[13] Stefan Nowy, Wei Ren, Julia Wagner, Josef A. Weber and Wolfgang Brütting, Proc. Of SPIE – Organic Light Emitting Materials and Devices XIII, ed. Franky So, 7415 (2009) 74150G
[14] P. Stallinga, Electrical Characterization of Organic Electronic Materials and Devices, (2009) Jonh Wiley & Sons Ltd, UK