Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thin Solid Films 498 (2006) 244 – 248

www.elsevier.com/locate/tsf

Short-diode like diffusion capacitance of organic light emission devices

Mei-Na Tsai [a,b], T.C. Chang [a,e,*], Po-Tsun Liu [c], Chung-Wen Ko [d], Che-jen Chen [d], Kang-mien Lo [b]

[a] *Department of Physics and Institute of Electro-Optical Engineering, Center for Nanoscience and Nanotechnology, National of Sum Yat-sen University, 70 Lien-hai Road, Kaohsiung, Taiwan*
[b] *Yung Ta Institute of Technology and Commerce, Taiwan*
[c] *Department of Photonics and Display Institute, National Chiao Tung University, Taiwan*
[d] *AU Optronics Corporation, L1 Fab, OLED Department, Taiwan*
[e] *National Nano Device Laboratories, 1001-1 Ta-Hsueh Rd., Hsin-chu, Taiwan*

Abstract

A prototypical organic light-emitting diode (OLED), anode/organic layers/cathode, is investigated via bias-dependent capacitance measurement of two-layer (HTL/ETL) and four-layer (HIL/HTL/EML/ETL) structure at low frequency. As applied voltage was larger than the built-in voltage, the capacitance is augmented by diffusion capacitance with increasing the forward bias voltage. In contrast, the capacitance dropped quickly. It is possibly due to the voltage drop in the bulk and conductivity modulation occurred by high carrier concentration for much higher forward biases, eventually showing negative for two-layer OLEDs. We infer that the phenomena were resulted from the extremely thin OLED structure, just like short $p-n$ semiconductor diodes. This diffusion capacitance exhibiting like short-diode behavior also can be measured in $C-V$ curves of single-layer structure OLED.

Keywords: OLED; Diffusion capacitance; Non-combination carriers

1. Introduction

The huge interest in new display technologies has greatly stimulated research on small molecule based organic light-emitting diodes (OLEDs) in the last years. Since the new materials were found, and device structures and injection contacts have been improved, in the meanwhile the products with OLED displays are on the market, such as a multicolor display in a car radio (Pioneer, Samaung, etc.) and a monochrome display in a cellular phone. Nevertheless, many scientific and technological processes are still not understood and worthy to do research on.

In this work, we will measure bias-dependent capacitance ($C-V$) characteristics of blue doped single-layer (EML), two-layers (HTL/ETL) and four-layers (HIL/HTL/EML/ETL) organic light emission devices. Current–voltage ($I-V$) and capacitance–voltage ($C-V$) characteristics of such OLED devices will also be analyzed to explore the carrier extraction mechanism.

2. Experimental details

OLED devices were fabricated using indium tin oxide (ITO ≈ a thickness of 75 nm) coated glass. A 30-nm-thick single-layer blue doped emitter, two-layer 20-nm-thick HTL as hole-transporting layer and 30-nm-thick ETL as electron-transporting were subsequently deposited onto previously structured ITO. In addition, four-layer OLEDs consists of 150 nm HIL/30 nmHTL/60 nm EML/30 nm ETL was fabricated for comparison. The LiF/Al cathode with an area of 0.2 cm^2 was formed with 1 nm-thick LiF and 150-nm-thick Al deposition. Four identical devices were made

---

* Corresponding author. Department of Physics and Institute of Electro-Optical Engineering, Center for Nanoscience and Nanotechnology, National of Sun Yat-sen University, 70 Lien-hai Road, Kaohsiung, 804, Taiwan. Tel.: +886 7 5252000x3708; fax: +886 7 5253709.

E-mail address: tcchang@mail.nsysu.edu.tw (T.C. Chang).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.07.104

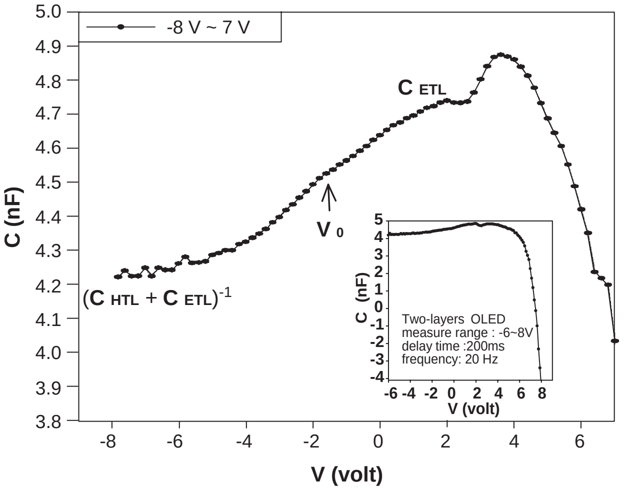

Fig. 1. Capacitance of an ITO/HTL (20 nm)/ETL (30 nm)/LiF (1 nm)/Al (150 nm) OLEDs as a function of dc bias.

simultaneously on the same glass substrate. After fabrication, the devices were immediately transferred into a nitrogen-filled glove box and encapsulated under a metal cover containing a desiccant.

C–V measurements were carried out with a Agilent 4284A precision LCR meter, a dc bias with a sinusoidal ac signal of 25 mV amplitude and 20 Hz or 30 Hz frequency was used. I–V characteristics were measured with a Hewlett Packard parameter analyzer HP 4156C, both 4284A and 4156C are connected to HP E5250A low leakage switch mainframe, and then link to dark box. So, OLEDs were protected from environment light illumination during measurements. All measurements were performed at room temperature. The transition between two capacitances is not altogether sharp. To enable comparison of the values obtained under different structure OLEDs, the "transition voltage" was identified arbitrarily with the inflection point of the C–V curve in the transition region.

3. Experimental results

3.1. Bias-dependent capacitance

Fig. 1 shows C–V characteristic of an OLED device with two-layer ITO/HTL/EML/LiF/Al. As reported by Kondakov et al. [1] and Brûtting et al. [2], they explained the transition in the C–V curve. For high reverse bias ($V \ll V_{\mathrm{bi}}$), the devices behave like an insulating dielectric sandwiched between two electrodes, because of the location of the immobile ("fixed") negative charge present in the OLED. At a certain applied voltage (i.e. transition voltage V_0), the electric field in the HTL vanishes, but the electric field in the ETL remains negative. Thus the OLED behaves as a capacitor with a dielectric layer, exhibiting only the capacitance of the ETL [1,2]. The "transition voltage" was identified arbitrarily with the inflection point of the C–V curve in the transition region. While the applied voltage is equal to V_{bi}, the electric field in the ETL vanishes. In addition, the electric field in the ETL becomes positive and electrons will be injected from the cathode [1,2]. Nevertheless, there is still a special capacitance peak when applied voltage is larger than built-in voltage V_{bi}, which has not been studied by other researchers so far. Comparing to the capacitance of p–n diode, Laux and Hess [6,7] have shown the diffusion capacitance has a peak capacitance for short-diode, and the peak of capacitance varies sharply, finally being negative around the built-in voltage. And our study indicates the same negative value of capacitance at sufficiently large voltage bias, as shown in the inset of Fig. 1. The capacitance is measured in response to a sine wave with 25 mV of amplitude and frequency 30 Hz. The inflection point (arrow) is identified with the transition voltage V_0. There is a peak of short-diode diffusion capacitance at 2.1–3.5 V. The inset shows negative capacitance at sufficiently large bias for the same sample at measure frequency 20 Hz.

The four-layers OLED devices: a HIL material between ITO/HTL and a EML between HTL/ETL are beneficial to enhance charge injection at the interfaces and the electro-

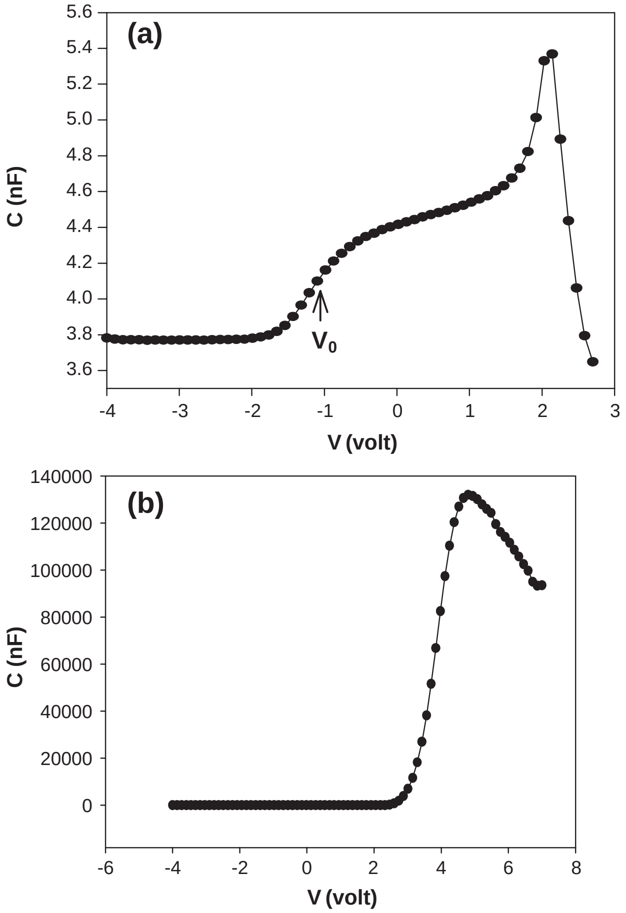

Fig. 2. C–V characteristics for (a) an ITO/HIL (150 nm)/HTL (30 nm)/EML (60 nm)/ETL (30 nm)/LiF (1 nm)/Al (150 nm) four-layer device; (b) an ITO/EML (30 nm)/LiF (1 nm)/Al (150 nm) single-layer OLEDs.

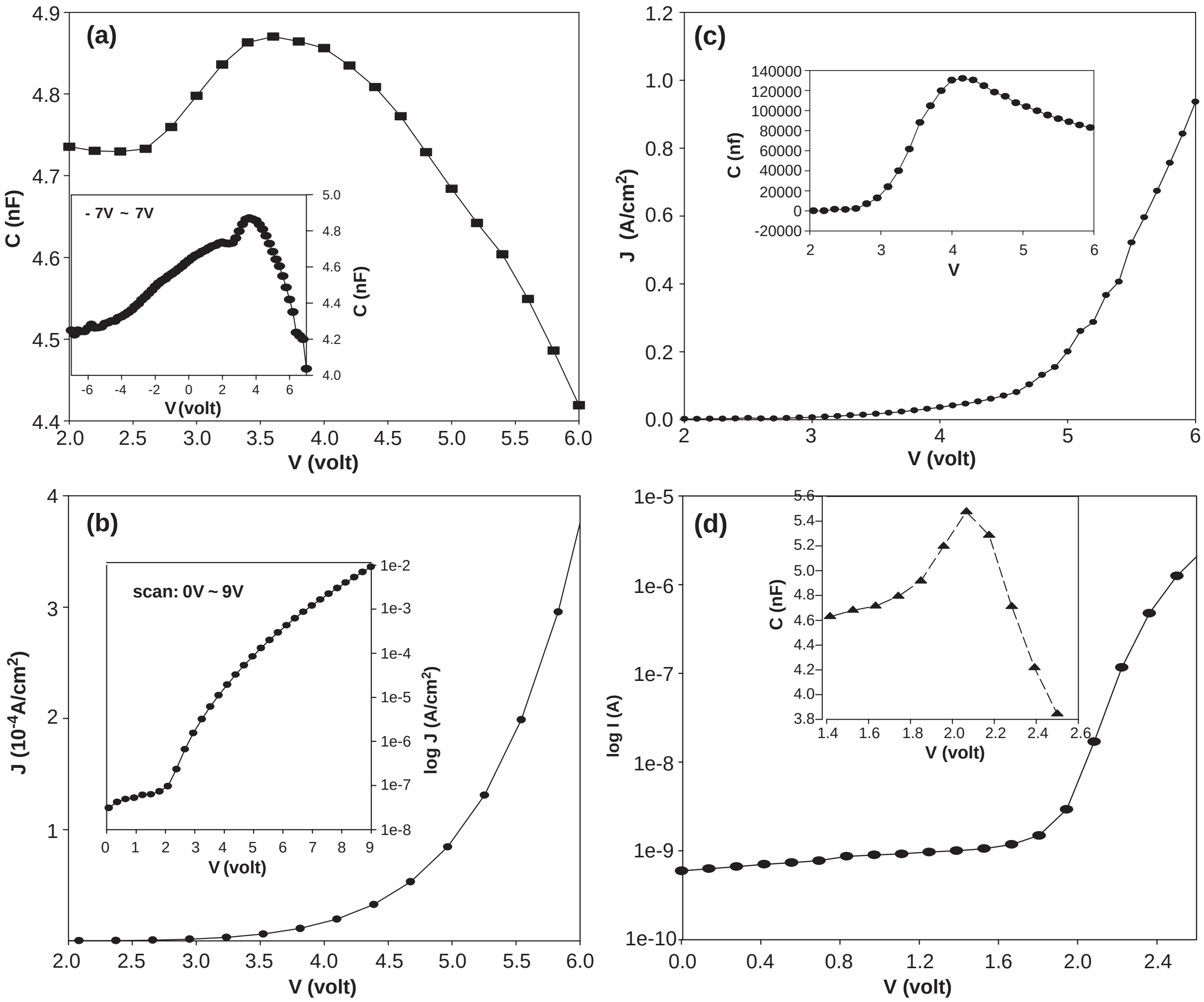

Fig. 3. Comparison of short-diode like $C-V$ ((a) inset is the whole curve) and $I-V$ (b) characteristics of ITO/HTL (20 nm)/ETL (30 nm)/LiF (1 nm)/Al (150 nm) two-layer OLEDs for the same range of bias. (c) $C-V$ and $I-V$ for single-layer OLEDs. (d) $C-V$ and $I-V$ for four-layer OLEDs.

luminescence color. Fig. 2(a) shows $C-V$ characteristics of the four-layers OLED device, which still exists a transition voltage V_0, and the electric field in the HIL/HTL vanishes instantaneously. The OLED behaves as a series connection of capacitors, with EML and ETL layers. Finally, the field in the EML and ETL becomes positive and the cathode also begins to inject electrons simultaneously. Also, a short-diode like diffusion capacitance peak is observed. The $C-V$ curve for a one-layer device is the extra evidence. Owing to no HTL, no transition voltage occurred in single-layer device. Capacitance changes from C_{EML} to short-diode like diffusion capacitance. The amazing peak capacitance can't be ignored. See Fig. 2(b).

3.2. $I-V$ characteristics

For two-layers structure OLEDs. Comparing the same applied voltage range for current and capacitance, those curves indicate that diffusion capacitance occurred in on-current generation. The behavior of single-layer and four-layer OLED is alike. As shown in Fig. 3. For OLEDs, the

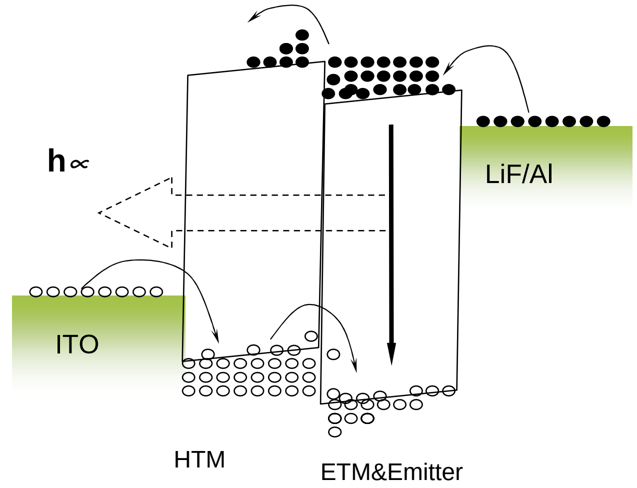

Fig. 4. Double-layer device, with holes injected from ITO, result in minority holes stored in EML layer, and minority electrons stored in HTL layer.

“turns on” injection condition must be that V_{appl} nearing or larger than V_{bi}. Then holes can be injected from ITO to HTL and diffuse to ETL. The non-recombine excess holes result in a charge storage capacitance in ETL layer, and excess electrons results in a charge storage capacitance in HTL layer. See Fig. 4. This will finally lead to the very little stored charges just like minority carriers storing in p–n diodes. So we suggest that the charge storage capacitance of OLEDs is similar to short-diode diffusion capacitance.

4. Discussion

Discussing two-layer structure OLEDs, as soon as injection condition turns on, the hole is injected from ITO to HOMO (the highest occupied molecular orbital) of HTL, then transport through HTL, across HTL/ETL interface, subsequently undergoing radiative or non-radiative recombination [3]. Then non-recombine excess holes were stored in ETL. Similar behavior of electrons was happening in HTL. Electrons were injected from LiF/Al to ETL’s LUMO (the lowest unoccupied molecular orbital). According to the model of OLED established by Ruhstaller [8,9], bipolar charge transport with field-dependent mobilities $\mu(E)=\mu_0\exp\left(\sqrt{E/E_0}\right)$ and Langevin recombination $r=\left(\frac{q}{\varepsilon}\right)\left(\mu_{\mathrm{e}}+\mu_{\mathrm{p}}\right)$. Consider Poisson’s equation $\mathrm{d}E(x)/\mathrm{d}x=\left(\frac{q}{\varepsilon}\right)\left(p(x)-n(x)\right)$ and displacement current $J_{\mathrm{d}}=\frac{\mathrm{B}}{\mathrm{B}t}[\varepsilon E(x)]$. For the two-layer device shown in Fig. 5, we can integrate hole-current continuity equation from 0 to c and electron-current continuity equation from $-a$ to 0. Thus the total current J_{t}

$$\begin{aligned} J_{\mathrm{t}} &= J_{\mathrm{n}}(0)+J_{\mathrm{p}}(0)+J_{\mathrm{d}}(0) \\ &= \underset{\text{term 1}}{q\int_{-a}^{c} r\mathrm{d}x} + \underbrace{q\int_{-a}^{0}\frac{\partial n}{\partial t}\mathrm{d}x+q\int_{0}^{c}\frac{\partial p}{\partial t}\mathrm{d}x}_{\text{term 2}} \\ &\quad + \underset{\text{term 3}}{q\int_{0}^{c}\frac{\partial(n-p)}{\partial t}} + \underbrace{J_{\mathrm{p}}(c)+J_{\mathrm{n}}(-a)}_{\text{term 4}} + \underset{\text{term 5}}{J_{\mathrm{d}}(c)} \end{aligned} \qquad (1)$$

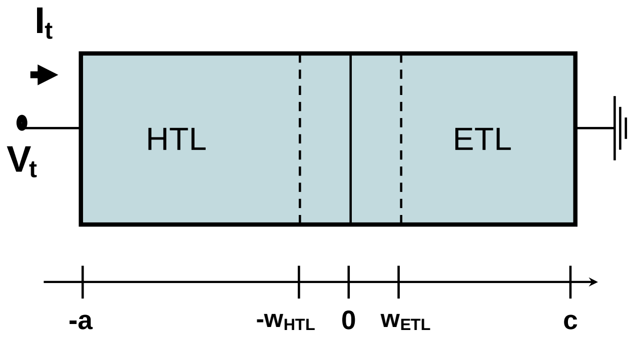

Fig. 5. Double-layer device, the total diode length is $c+a$. The depletion width is W which extends from $x=-W_{\mathrm{HTL}}$ to W_{ETL}. The junction at $x=0$ separates regions of HTL and ETL.

Eq. (1) contains both dc and ac information. In comparing equation to the p–n diode current equation which supposed by Laux and Hess [6], they are almost the same one. All terms of Eq. (1) contributed to the small-signal ac diode capacitance. Term 1 is a recombination of injected minority carriers at the neutral (bulk) p-base or n-base. Term 2 is local minority carriers built up in neutral (bulk) base or depletion region. Term 3 is the depletion capacitance. Term 4 is the boundary conditions. Term 5 is generally so small as to be negligible. The sum of the terms 1, 2, 4, 5 gives exactly the diffusion capacitance at low frequency limit. For short-base diode, since the minority carrier’s diffusion lengths are much longer than the total length, term 1 is small. Thus, only term 2 and term 4 contribute diffusion capacitance to short-base diode. The physics of term 2 is capacitive because it always yield positive contributions to the sum. While term 4 yields negative contributions, their physics are inductive. Due to minority carriers delay between injection into the neutral regions and arrival at the contacts, the collection leads to a current which lags behind the junction voltage resulting in an inductive effect, captured by term 4. The consequence is only a portion of the charge injected into the base is reclaimable. The reclaimable charge is 2/3 of the total stored charge in p–n diode [5–7].

In OLEDs, as applied voltage nearing V_{BI}, it is low-injection condition, the electric field in HTL or/and ETL vanish, few carriers diffused from one side across HTL/ETL interface and stored in the other side of OLEDs. The non-recombine excess minority might increase the local concentration (term 2) or leave via the contact (term 4). Thus the short-diode capacitance was very fast increased by carriers storage (term 2), but the value wasn’t equal total storage capacitance because of term 4. While increasing the forward bias, the capacitive behavior becomes weaker gradually and the inductive behavior becomes more obvious gradually. Thus negative term4 contribute larger to be comparable with positive term 2. Thus, total capacitance reduces. The capacitance reduces to zero when increasing enough forward bias.

Why the capacitance becomes negative finally at large forward bias, the voltage drop in the neutral (bulk) regions may be the reason for negative term 4 with ultimate growing largely to dominate positive terms 2 which is so called inductive behavior result. The physics is: the voltage drop in the neutral (bulk) regions enlarges at larger forward bias. The injecting minority carriers are significantly influenced by the electrical field there, the electrical field in neutral (bulk) region will serve to sweep the carriers out of the contact faster than diffusion [6]. Term 4 becomes more negative. To evaluate the more accurate current component, it’s better to consider conductivity modulation [7]. Conductivity modulation effects is that the resistance of the diode bulk drops as the carrier concentrations reach their high injection values causing the diode voltage to fall [4,5].

Single-layer OLEDs could be compared to p^{+}/n diodes, it also has diffusion capacitance. The capacitance of single-layer didn’t become negative, this can be ascribed to the larger parasitic effects due to four identical devices made simultaneously on the same glass substrate. Four-layer OLEDs can be measured the more distinct capacitive effect. But the capacitance of four-layer OLEDs does not drop to zero or even to negative value. It may be that parasitic capacitance can not be eliminated.

5. Conclusion

This work has shown that the non-combination carriers will result in diffusion capacitance like a short-diode. In comparison with the electrical current equations of OLEDs and the ac equivalent circuit model proposed by Steven E. Laux, it has been indicated that the short base diode exhibits a peak capacitance and drops sharply. The capacitive phenomenon is attributed to the storage of carriers. The inductive effect came from the lag between carrier's injection and collection. Owing to the voltage drop in the bulk regions and high carrier concentration at large forward biases, the capacitance eventually became negative. For single-layer, two-layer and four-layer OLEDs, the peak capacitance of OLEDs like short-diode can be measured at low frequency.

Acknowledgments

This work was supported by the Republic of China National Science Council through grant No. NSC-94-2120-M-110-005.

References

[1] D.Y. Kondakov, J.R. Sandifer, C.W. Tang, R.H. Young, J. Appl. Phys. 93 (2003) 1108.
[2] W. Brűtting, H. Riel, T. Beierlein, W. Riess, J. Appl. Phys. 89 (2001) 1704.
[3] L.S. Hung, C.H. Chen, Mater. Sci. Eng., R Rep. 39 (2002) 143.
[4] M.A. Green, J. Shewchun, Solid-State Electron. 17 (1974) 941.
[5] J.J.H. van den Biesen, Solid-State Electron. 33 (1990) 1471.
[6] Steven E. Laux, K. Hess, IEEE Trans. Electron Devices 46 (2) (1999) 396.
[7] Ben G. Streetman, Sanjay Banerjee, Solid State Electronic Devices (2000).
[8] B. Ruhstaller, S.A. Carter, J. Appl. Phys. 89 (2001) 4575.
[9] Michel Schott, Appl. Phys. IV (2000) 381.