

Memory effect from charge trapping in layered organic structures

Sung Hoon Kang, Todd Crisp, Ioannis Kymissis, and Vladimir Bulović^{a)}

Laboratory of Organic Optics and Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 15 July 2004; accepted 29 September 2004)

We demonstrate organic light emitting devices (OLEDs) with a charge trap layer that show memory behavior. These OLEDs demonstrate that organic heterojunction structures can controllably trap and release electronic charges. The trap layer is either 5-nm-thick clustered silver islands, or a 10-nm-thick organic laser dye DCM2 ([2-methyl-6-[2-(2,3,6,7-tetrahydro-1*H*, 5*H*-benzo[*i,j*]quinolizin-9-yl)-ethenyl]-4*H*-pyran-4-ylidene] propane-dinitrile) doped into TPD (*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine). Predictions of the energy band structure indicate that both DCM2 sites and the metal islands can trap charge, consistent with the measured current–voltage characteristics. Trap sites are charged by applying reverse bias over the OLEDs. For devices with DCM2 traps we observe quenching of DCM2 photoluminescence upon charging, which allows us to quantify the charged trap density as approximately 10% of the trap sites or 10^{18} cm⁻³. From time resolved measurements we observe that the charge retention time exceeds 2 h. © 2004 American Institute of Physics. [DOI: 10.1063/1.1819991]

Structural disorder in amorphous organic thin films can result in the presence of localized electronic states which can trap and store charge in equilibrium.^{1,2} The presence of such trapped charges can dominate the current–voltage (*I*–*V*) characteristics of organic devices because of a relatively low density of intrinsic free charge carriers in organic solids.³ For example, recent studies of organic bistable memories proposed that charge trapping process can control the active state of the device.^{4,5} In this letter, we similarly investigate the charge trapping process in device structures that in forward bias perform the function of organic light emitting devices (OLEDs), while in the reverse bias store charge, which can be interpreted as a memory event. We demonstrate that charge storage can be engineered in active organic electronic devices, and quantify the electrical charge density from the room temperature optical measurements and *I*–*V* characteristics.

We first investigate doped organic light emitting devices consisting of organic layer (material 1)/trap layer/organic layer (material 1)/organic layer (material 2) between an anode and a cathode. In Fig. 1(a) we use *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as material 1 and aluminum tris (8-hydroxyquinoline) (Alq₃) as material 2. The trap layer is a mixture of 95% by weight TPD and 5% laser dye [2-methyl-6-[2-(2,3,6,7-tetrahydro-1*H*, 5*H*-benzo[*i,j*]quinolizin-9-yl)-ethenyl]-4*H*-pyran-4-ylidene] propane-dinitrile (DCM2) (available from Exciton, Inc., Dayton, OH, under brand name LD688) deposited using vacuum co-evaporation. On top of the organic materials, a composite Mg:Ag (10:1 mass ratio) and a Ag electrode is deposited, without breaking vacuum, through a shadow mask, resulting in circular device area of 0.78 mm². All layers were deposited by thermal evaporation at pressure of less than 2×10^{-6} Torr. The thin film thickness was monitored by quartz crystal monitors, which were calibrated using a Tencor P-10 profilometer.

^{a)}Electronic mail: bulovic@mit.edu

Figure 1(a) shows the *I*–*V* characteristics of the device sketched in the figure measured using Agilent 4156C semiconductor parameter analyzer under ambient conditions. The shape of each *I*–*V* response is repeatable and depends on the bias at which the sweep is started. By comparing the *I*–*V* characteristics we find that current spikes at 1 V forward bias are observed only when the device is first subjected to a

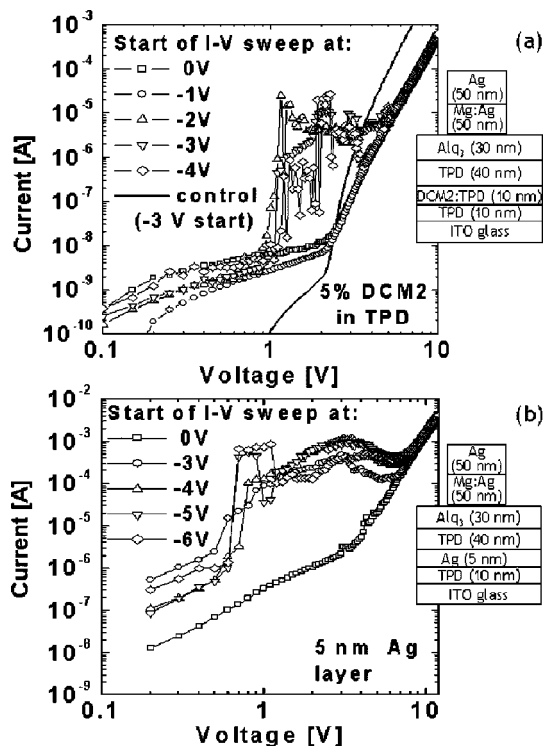


FIG. 1. The current–voltage characteristic and the structure of sample devices: (a) 10-nm-thick 5% DCM2 doped TPD trap layer device, (b) metal-trap device consisting of 5-nm-thick Ag nanoclustered trap layer. The *I*–*V* characteristics were measured by an Agilent 4156 C semiconductor parameter analyzer under ambient conditions. The legend indicates the voltage at which the sweep was started.

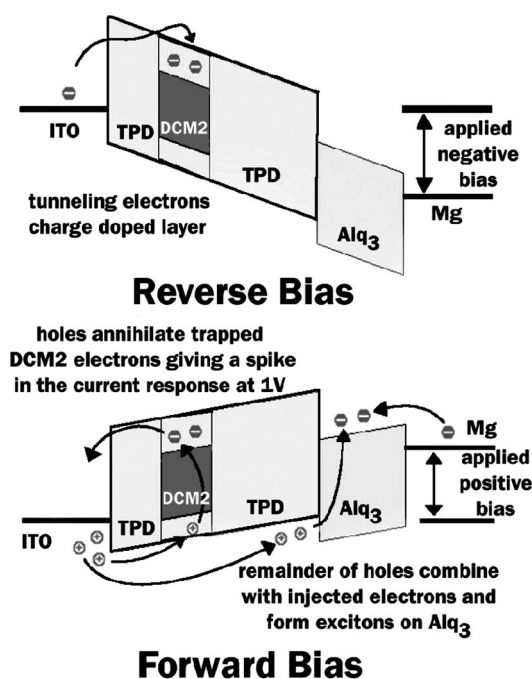


FIG. 2. Proposed operation mechanism of Fig. 1(a) devices. The expected energy band diagrams are not drawn to scale.

reverse bias of at least -2 V. To ensure that the device is in the same initial state, before every sweep that started at reverse bias, we performed a sweep that started at 0 V bias. Comparing this I - V behavior to a control device, which does not have the doped layer but has the same total thickness of the TPD layer, we note that the control device did not show the current spike for sweeps that started at reverse bias.

From a series of experiments using different charging time, we observe that the voltage at which the current spike occurs is lowered if we first apply reverse bias for a few seconds prior to measuring the I - V sweep. This suggests that precharging time determines the amount of injected/stored charge in the charge trapping layers, and hence influences the current response in the forward bias sweep. For I - V sweeps that start at 0 V, the doped device compared with a TPD/Alq₃ OLED of same thickness, has about 10% higher luminescence quantum efficiency, possibly due to a more balanced hole and electron injection into the device.⁶ The operating voltage, however, is higher in the doped device than in the OLED with the current up to ten-fold smaller at the same voltage.⁷

A schematic band diagram shown in Fig. 2 illustrates the proposed operating mechanism of the charge trapping device of Fig. 1(a). When the device is reverse biased, electrons injected from the anode charge the trap layer. If we then apply a forward bias, holes from the anode recombine with the trapped DCM2 electrons generating the current spike. The remainder of the injected holes combine with injected electrons from the cathode to form excitons near TPD/Alq₃ interface. By changing the magnitude of the reverse bias, we can control the amount of stored charge in the trap layers and therefore the magnitude of the spike current. If the magnitude of the reverse bias is too small, no current spike in forward bias is observed as the reverse bias voltage is insufficient to facilitate electron injection over the anode/TPD interface. If too great reverse bias is applied, the net amount of stored negative charge is reduced due to hole injection at the

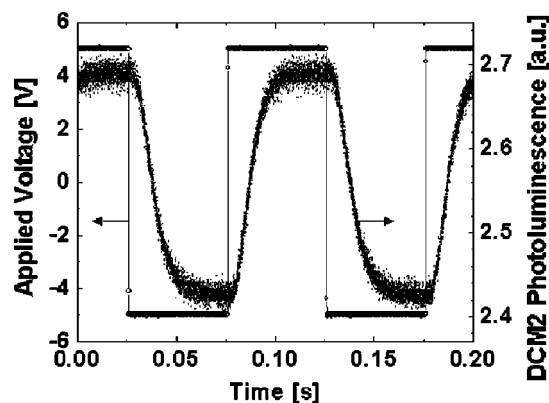


FIG. 3. The change in the DCM2 photoluminescence intensity with the change in the device bias. The devices were excited with a chopped $\lambda = 532$ nm light. The chopper frequency was in the range of 620–650 Hz. The OG-530 optical filter (Ealing Catalog, Inc., Rocklin, CA) was used to selectively detect the red DCM2 luminescence.

cathode. This leads to a decreased spike current response for reverse biases of < -5 V.

In order to verify that charges are stored in the DCM2:TPD trap layer of the device in Fig. 1(a), we measured DCM2 photoluminescence (PL) for charged and discharged trap layer. The PL measurement was performed by exciting the device with a chopped $\lambda = 532$ nm wavelength light generated by frequency doubled Nd:YAG laser. This wavelength light is only absorbed by DCM2, resulting in red PL signal that is detected by Newport 818-SL photodiode connected to Stanford Research SR 830 lock-in amplifier. The lock-in amplifier is referenced to the light chopping frequency, and the response is recorded on the Tektronix TDS 300B oscilloscope. Concurrently, a square wave bias was applied over the device using Agilent 33250A arbitrary wave form generator. When the trap layer is charged (-5 V applied in Fig. 3), we observe that the DCM2 PL intensity decreases. This is strong evidence that charge is stored in the DCM2 traps since luminescence of negatively charged DCM2 molecules is quenched via the Auger process. DCM2 PL intensity is recovered in discharged devices ($+5$ V applied bias in Fig. 3). Assuming that only charged molecules are PL quenched with no influence on the neighboring molecules, the $\sim 10\%$ change in the PL intensity implies the same percentage of charged DCM2 sites or 10^{18} cm⁻³ (the density of the DCM2 is 1.1 g/cm³, and the molecular weights of DCM2 and TPD are 355.2 and 516.3 g/mol, respectively). This is an upper limit on the number of charged sites since Förster transfer from uncharged to charged DCM2 molecules can magnify the PL quenching.

The above-mentioned model suggests that replacing the DCM2 dopant with a metallic trap could result in higher charge storage due to the high density of the electronic states in metal films, and a possibly deep trap depth for the metal traps that have the Fermi level energy aligned with the middle of the TPD band gap.

We made the metal-trap devices by depositing 5 nm of Ag on top of TPD, Fig. 1(b). When a thin Ag film is deposited on top of the organic layer, it forms metal clusters similar to the earlier studies of Al on Alq₃.⁵ The atomic force microscopy images show Ag cluster average size on the order of 10 nm. As expected, the metal-trap devices exhibit the memory behavior with the I - V characteristics showing an increased charge current density through the metal-trap de-

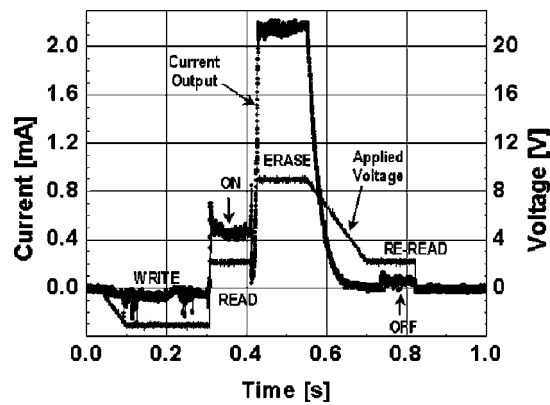


FIG. 4. Write-Read-Erase-Read cycle of the Fig. 1(a) device. The writing, reading, and erasing voltages are -3 , 2 , and 9 V, respectively.

vices, as compared to the DCM2-trap devices [Fig. 1(b)]. In forward bias, however, the peak of the electroluminescence spectrum is shifted due to the microcavity effects induced by the reflection at the 5 nm Ag layer.

Figure 4 shows the time resolved I - V characteristic of the DCM2:TPD trap layer device. The write-read-erase-reread cycles were recorded with an oscilloscope using an arbitrary wave form generator and a Keithley 428 current amplifier. The difference between the read and re-read currents demonstrates the “on” and “off” state of the bit stored in the doped organic light emitting device. We measured the retention time of the device by delaying discharge. After applying negative bias, we waited for up to 2 h before “reading” the device with a I - V sweep, and we still observed the current spike associated with charge storage.

Finally, in order to see the effect of different doping concentrations, we fabricated samples with 10% and 20% DCM2 doped TPD trap layer, and compared the device characteristics with the 5% DCM2 doped device. For increased doping concentration, a higher forward bias is needed to extract trapped charges from the device. In the case of the highly polar DCM2 the energy structure changes with doping possibly resulting in deeper trap energies when matched to TPD.² The retention time of the device also increases as we increase the doping concentration consistent with the deeper trap assertion.

In conclusion, this letter demonstrated two organic heterojunction structures, which can controllably trap and release electronic charges. The energy band structure and current-voltage characteristics from these devices strongly indicate that both DCM2 sites and the metal trap layer are trapping electrons under reverse bias. This has been experimentally verified by PL quenching measurements for the organic trap layer device with the maximum charge density in the trap layer on the order of 10^{18} cm^{-3} . For a fixed charging time, the magnitude of applied reverse bias determines the amount of stored charge in the trap layer, influencing the current response in the forward bias sweep. When the organic trap layer is replaced with a metal layer, the higher density of trap states in the metal layer results in higher discharge current. From time resolved measurements, we also demonstrated that the trapping layers within an OLED structure allow storage of information on the OLED by applying reverse bias on the device. The retention time of the device is in excess of 2 h. In such manner, OLED display pixel arrays can be used as memory arrays that, for example, store information when the display is dormant.

This work is supported in part by MARCO Focused Research Center on Materials Structures and Devices, which is funded in part by MARCO under Contract No. 2003-MT-887 and DARPA under Grant No. MDA972-01-1-0035 and in part by the MRSEC Program of the National Science Foundation under Award No. DMR 02-13282. S.H.K. appreciates the financial support from the Republic of Korea (ROK) Ministry of Information and Communication (MIC). The authors are grateful to Alexi Arango for his assistance in time resolved measurements of the memory behavior.

¹M. A. Lampert, *Phys. Rev.* **103**, 1648 (1956).

²C. F. Madigan and V. Bulovic, *Phys. Rev. Lett.* **91**, 247403 (2003).

³P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin, and M. E. Thompson, *J. Appl. Phys.* **79**, 7991 (1996).

⁴L. P. Ma, J. Liu, and Y. Yang, *Appl. Phys. Lett.* **80**, 2997 (2002).

⁵L. D. Bozano, B. W. Kean, V. R. Deline, J. R. Salem, and J. C. Scott, *Appl. Phys. Lett.* **84**, 607 (2004).

⁶G. G. Malliaras and J. C. Scott, *J. Appl. Phys.* **85**, 7426 (1999).

⁷S. Naka, H. Okada, H. Onnagawa, Y. Yamaguchi, and T. Tsutsui, *Synth. Met.* **111**, 331 (2000).