Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.386-387

Memory Effect of Device Based on a Conjugated Donor-Acceptor Copolymer

Y. Song[1], Q.D. Ling[2], Chunxiang Zhu[1], E.T. Kang[2], D.S.H. Chan[1], Y.H. Wang[3], D.L. Kwong[3]

[1]SNDL, Dept of Electrical and Computer Engineering, National University of Singapore
10 Kent Ridge Crescent, Singapore (Email: elezhucx@nus.edu.sg)
[2]Dept of Chemical and Biomolecular Engineering, National University of Singapore, Singapore
[3]Institute of Microelectronics, Singapore

Introduction

With the advancement in information technology, the semiconductor industry faces scaling problems and physical limitations on device components [1]. Developments of new materials technology to resolve these problems is emergent. For this reason, organic materials have been aggressively explored for semiconductor device applications. It has been widely reported that different kinds of electronic devices, such as light-emitting diodes [2], field-effect transistors [3], logic gates [4], optocouplers [5], photodetectors [6], and lasers [7], can be derived from organic materials. Very recently, organic memories have received a great deal of attention due to their simple structure, good scalability, CMOS compatibility, and potentially, low cost. Several kinds of organic molecular materials have been found to exhibit memory effects [8-11]. Polymer memory devices are potentially far less expensive to make than those based on organic molecular materials. Polymer circuits, for example, can be deposited on substrates via ink-jet printing or spin-coating. In this paper, we report memory effect in a MIM sandwich structure based on a copolymer consisting of electron-donor (fluorene) and acceptor (Eu complex) groups. The molecular structure of the new copolymer, PF8Eu, is shown in Fig. 1.

Experimental

The synthetic route for the conjugated copolymer containing 9,9'-diethylhexylfluorene and europium complex-chelated benzoate units in the main chain is shown in Fig. 2. It involved three steps: 1) a copolymer of 2,7-bis(trimethylene boronate)-9,9-diethylhexylfluorene and methyl 3,5-dibromobenzoate was synthesized through a palladium-catalyzed Suzuki coupling reaction (P1); 2) the copolymer was then hydrolyzed to provide the active carboxylic ligands in the main chains (P2); and 3) the polymeric ligands, together with DBM and 1,10-phenanthroline (phen), chelated the highly reactive europium triisoproxide to form the desirable copolymer complex (P3 or PF8Eu). The basic device structure is shown in Fig. 3 The indium-tin-oxide (ITO) coated glass substrate was patterned to 2mm wide and then cleaned with DI water, acetone and isopropanol, in that order, in an ultrasonic bath for 20 min. The ITO is defined as cathode. A toluene solution of PF8Eu (8mg/ml) was spin-coated on the ITO, followed by solvent removal in a vacuum chamber at 10^{-5} Torr for 9 hours. Finally, the top Al electrode with line-width of 0.2mm was thermally evaporated at a pressure of $\sim 10^{-7}$ Torr through a shadow mask. The shadow mask was used to pattern and define the top electrode area. The top and bottom electrodes were aligned perpendicularly, so that the active area was defined by a crossed area of 2mm$\times$0.2mm. The thickness of the polymer film is 50 nm, as measured by a profiler. Electrical measurements were carried out with an HP 4156A semiconductor parameter analyzer in a dark chamber. All electrical measurements were conducted under ambient conditions without any encapsulation.

Results and Discussion

The memory effect of the device is observed in the J-V (current density - voltage) curve of the Al/PF8Eu/ITO sandwich device. Fig. 4 shows a typical J-V characteristics of the device. It distinctively displays two conducting states. With an applied voltage on the as-fabricated device, the current increases slowly as the voltage increases. This is the low conductivity state (OFF-state). If the applied voltage further increases up to ~3V, a sharp increase in the current is observed, indicating the device transition from the low conductivity state (OFF-state) to a high conductivity state (ON-state). This transition from the OFF-state to the ON-state serves as the "writing" process for the memory device. After the device reaches to its high conductivity state, it remains in this ON-state even after turning off the power. The inset in Fig. 4 shows the ratio of the ON- to the OFF-state current as a function of applied voltage for the same sweep. An ON/OFF current ratio as high as 10^7 has been achieved. This feature promises a low misreading rate by precise control over the ON and OFF states. We have not found the condition to erase the ON-state of the device until now. The ON-state of the device is stable. A 1V stress was applied on the ON-state device and there is no significant degradation observed after 3 hours test. The origin of the electrical bistability in the device is still under investigation. To understand the mechanism of the memory effect, we measured the capacitance of the device under the same sweep as used in J-V measurement. The result is shown in Fig. 5. The ON-state capacitance is 2 orders of magnitude higher than that of the OFF-state. This implies that more charges are trapped in the device in the ON-state. Thus, the trapped charges are probably responsible for the memory effect in the present device. The detail mechanism of the memory effect will be reported shortly.

Summary

We have shown that MIM-structured devices, based on a donor-acceptor copolymer material (PF8Eu), exhibit electrical conductance switching behavior. The J-V characteristics of the device was measured and an electrical bistable phenomenon was observed. At a specified voltage, the device exhibited two conductivity states with an ON/OFF current ratio as high as 10^7. The device remained in either states even after the power is turned off and shows a memory effect.

Acknowledgement:
This work was supported by R-263-000-327-112 (NUS, Singapore) and IME/04-410004 (IME, Singapore).

References

[1] C. Li, et al, *Appl. Phys. Lett.*, **82**, 645 (2003).
[2] C.W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
[3] F. Garnier, R. Hajlaoui, A. Yassar, and P. Srivastava, *Science*, **265**, 1684 (1994).
[4] B. Crone, et al, *Nature*, **403**, 521 (2000).
[5] G. Yu, K. Pakbaz, and A.J. Heeger, *J. Electron. Mater.*,**23**, 925 (1994).
[6] G. Yu, K. Pakbaz, and A.J. Heeger, *Appl. Phys. Lett.*, **64**, 3422 (1994).
[7] N. Tessler, G.J. Denton, and R.H. Friend, *Nature*, **382**, 695 (1996).
[8] R. Sezi, et al, Proc. of *IEDM*, pp. 259, (2003).
[9] J. Chen, M.A. Reed, A.M. Rawlett, and J.M. Tour, *Science*, **286**, 1550, (1999).
[10] C.P. Collier, et al, *Science*, **289**, 1172, (2000).
[11] Z.J. Donhauser, et al, *Science*, **292**, 2303, (2001).

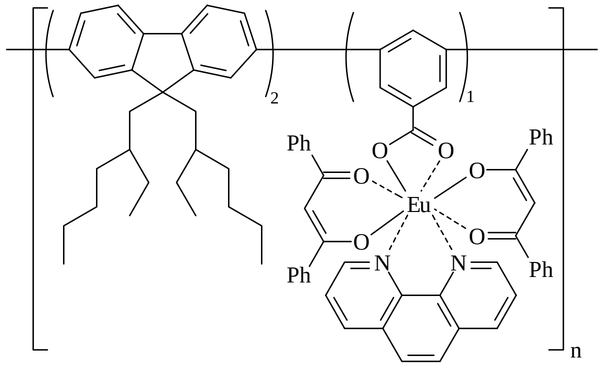

Fig. 1 The molecular structure of PF8Eu which consists of electron-donor (fluorene) and acceptor (Eu complex) groups.

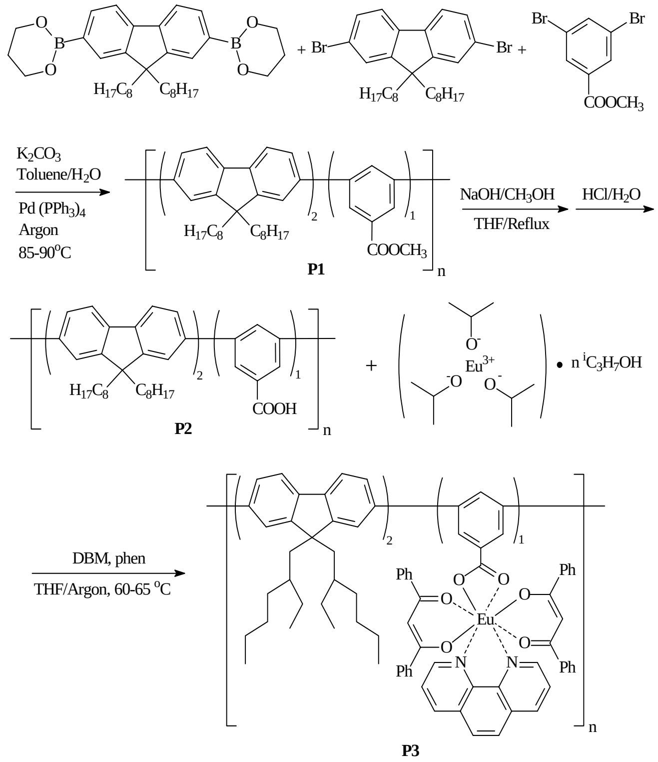

Fig. 2 Synthetic route for the copolymer containing fluorene and europium complex in the main chain.

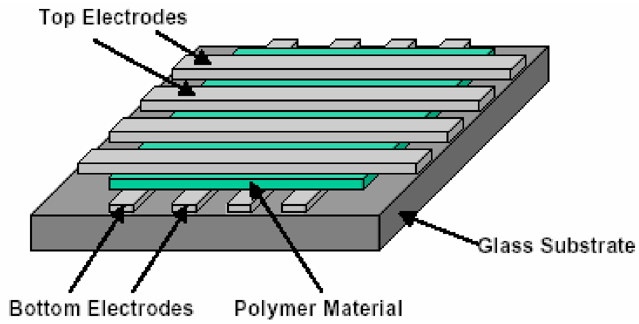

Fig. 3 Schematic diagram of the memory device consisting of a PF8Eu thin film sandwiched between an ITO coated substrate and aluminum top electrodes.

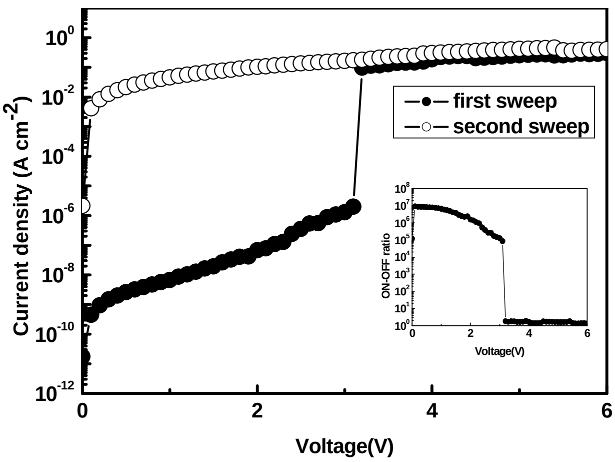

Fig. 4 A typical J-V characteristics of the Al/PF8Eu/ITO device. Voltage was swept from 0V to 6V. The inset shows the ON- to OFF- current ratio as a function of applied voltage for the same sweep.

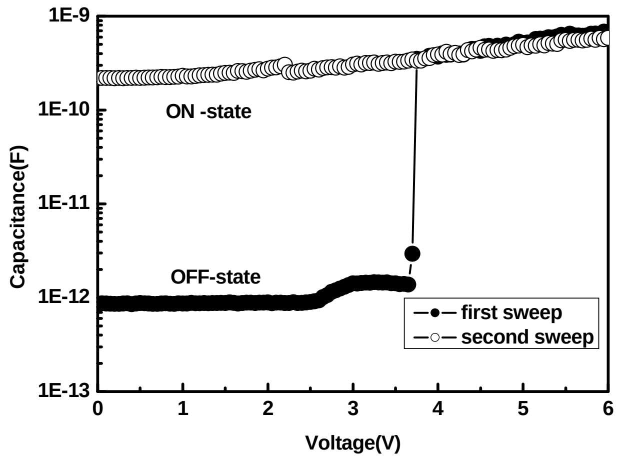

Fig. 5 A typical C-V characteristics of the Al/PF8Eu/ITO device, indicating more charges are stored under ON-state.