Structure and Process of Ink-Jet Printed Organic Memory

Chao-Feng Sung, Kuo-Tong Lin, Yuh-Zheng Lee, Je-Ping Hu, Kevin Cheng, Jane Chang, and Ti-Fa Ying, OES/Industrial Technology Research Institute, Hsinchu, Taiwan, R. O. C.; Yang Yang, Department of Materials Science and Engineering, University of California-Los Angeles, Los Angeles, California, USA

Abstract

An organic memory fabricated by ink-jet printing and thermal evaporation technique is reported. Typically, the device is formed with two buffer layers and one organic layer sandwiched between two metal electrodes. The resulting structure is glass substrate/ink-jet printed silver electrode/buffer layer/organic layer/buffer layer/copper electrode positioned in sequence. For the first electrode of the device, a solution with stable dispersions of nano-particles in a liquid vehicle was used as the printing ink. The ink contains surface modified ultra-fine particles that form stable colloids when dispersed in an appropriate solvent. This ink is jetted by a piezo ink-jet head to a pretreated glass and then thermal cured to afford a low resistive metal film. The width of each printing metal line is about 200 µm with acceptable roughness to be used as the first electrode of an organic bi-stable device (OBD). Experimental results showed that the organic memory device can be driven by voltage modulation, which causes the nonvolatile memory effect by controlling the Cu^+ ion concentration within the organic layer interposed between two metal electrodes. The memory-read operation is demonstrated when the Cu^+ concentration is swept to the positive electrode as the applied voltage scans from 0V to 3V. The observed on/off ratio can reach more than 10^5.

Introduction

Organic semiconductor devices have attracted considerable attention in recent year due to their potential advantages of flexibility, easy processing, low cost, and feasible large area fabrication by printing techniques. Several types of organic electronic and opto-electronic devices have been developed by use of organic functional materials as the active compound, for instance, organic light emitting diodes,[1,2] transistors,[3,4] solar cells[5,6] and memory devices[7-12] Silicon-based flash memory,[13] with a response time in the sub millisecond range, has been widely employed in nonvolatile semiconductor memories. There are two major applications of flash memories. One is applied as nonvolatile memory integration in logic systems, and the other is used as storing elements, such as memory boards or solid-state hard disks. As the market demands, it is beneficial to drive the electronic nonvolatile memory device much cheaper, so organic electrical bi-stable device (OBD) with easy manufacturing process is a promising alternative in this aspect. Recently, a new structure of copper based organic bi-stable device can also perform as a nonvolatile memory by controlling the Cu^+ ion concentration within the organic layer interposed between two metal electrodes.[14] In this paper, we report an approach to make the first electrode with nano-particles ink by ink-jet technique to replace the thermal evaporating process as the first step to a fully printing OBD. In addition, two buffer layers are used to keep the device more stable.

Treatment and Fabrication Processes

In this study, the structure of the organic bi-stable device (Cu-OBD) with ink-jet printing silver electrode is shown in Fig. 1. The bottom silver electrode was selected because of its low resistivity obtained after very short curing time, reliable inkjet printing behavior and good adhesion to glass, FR4 and PET, etc. The top copper electrode was selected due to its high diffusion coefficient. Material with low conductivity, good film formability, and stability such as Tris-8-(hydroxyquinoline) aluminum (Alq3) purchased from e-Ray is selected as the organic layer. A buffer layer (~4 nm thick), comprised of dielectric materials selected from such as lithium fluoride (LiF), aluminum oxide, vanadium oxide (V_2O_5), molybdic oxide (MoO_3) or tungsten trioxide (WO_3), was deposited between the organic layer and each one of the electrodes, respectively.

The glass substrates were cleaned sequentially by acetone, IPA and deionized water in ultrasonic bath. Ink-jet printing and vacuum thermal evaporation techniques were used for the electrode deposition. The ink jet 3G platform, developed by OES[15,16] and equipped with spectra SE-128 piezoelectric print heads, was used for discharging the silver nano-particles inks purchased from Cabot. The low resisitivity patterned silver electrode was obtained after being post baked at 100~350°C in air for 1~30 minute to sinter the pre-deposited precursor material. On this ink-jet forming electrode, the first buffer layer, the organic layer, the second buffer layer, and the top electrode (anode) were sequentially deposited by thermal evaporation without exposure to air. The substrate was transferred from one shadow mask to another in the nitrogen box for different patterns of the buffer/organic layers and the top electrode. The device area (0.1 mm*0.2mm) is defined by the overlap of the top and the bottom electrodes. The thickness of the buffer layer and the organic layer are 4 nm and 70 nm, respectively. During deposition, the vacuum of the chamber was kept at about 1×10^{-5} Torr. The current density–voltage (J–V) measurement was conducted on a HP 4155B semiconductor parameter analyzer and a KEITHLEY 2400 source meter.

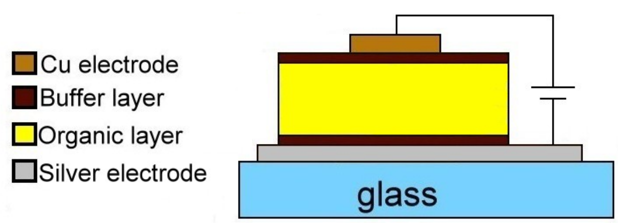


Figure 1. The structure of the Cu-based organic bi-stable device (Cu-OBD) with a silver bottom electrode

Results and Discussion

Ink-Jet Stability

There are three important factors dominating the jetting behavior of piezoelectric print heads, i.e. pulse waveform, pulse frequency and driving voltage. Appropriate waveform modulation and pulse frequency are necessary to be operated at suitable range to fit the operating range of the driving voltage for certain ink discharging. The jetting behavior can be observed by a strobe capturing system integrated in the 3G OES printing platform. The break-off behavior of the jettable silver nano-particles ink is captured in 70 microsecond and shown in Fig. 2. The velocity of the jetting drop is stable at about 6.4 m/s. With a standoff of 1 mm, we have successfully modulate the ink-jet printing parameters on Spectra SE-128 for silver nano-particles ink, and therefore uniform and continuous silver paste lines are obtained on a pre-cleaned glass substrate.

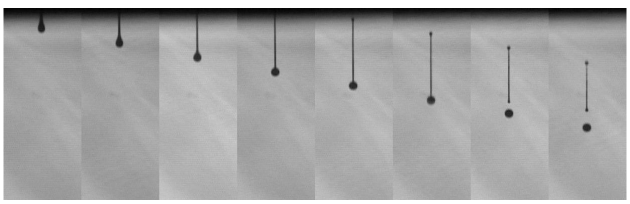
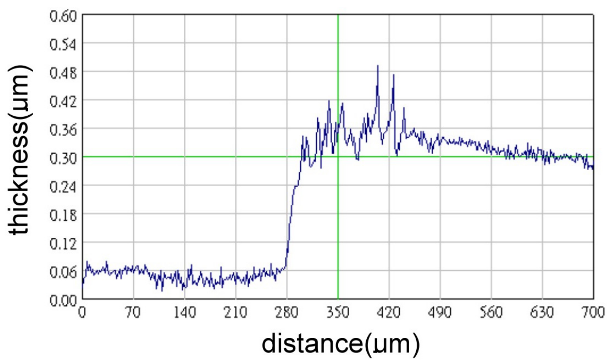
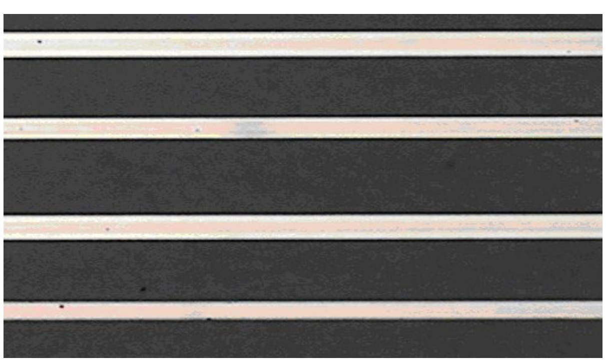


Figure 2. Observation of drop break-off behavior beneath an arbitrary nozzle.



(a)



(b)

Figure 3. (a) Profile of a sintered silver electrode formed by ink-jet printing; (b) Silver electrode on glass.

The Roughness of Ag Electrode by Ink-Jet Printing

Figure 3 shows the profile of a silver electrode formed by ink-jet printing, wherein the width and the average thickness of each Ag electrode are about 200µm and about 300nm, respectively. It is not smooth at the edge of the Ag electrode with obvious spikes. These spikes may result in the electric short of the fabricating OBD devices, so we deposited the first buffer layer to mitigate this phenomenon. The resulting sheet resistivity of the ink-jet electrode is about 100~200 mΩ after the patterned Ag nano-paste is sintered at temperature higher than 150°C.

Ink-Jet versus Evaporated Ag in OBD

The current density–voltage (J–V) curves of the OBD device with silver bottom electrode deposited by different process are shown in Fig. 4. For the evaporating case, the device structure is evaporated silver electrode/organic layer/buffer layer/copper electrode with only one buffer layer positioned between the organic layer and the copper electrode. Because the evaporated silver electrode is smoother than the ink-jet case with thickness of only 70 nm, the additional buffer layer located between the organic layer and the bottom silver electrode is not necessary to protect the device from electric short. When the applied bias is ramped from 0 to 8.5 V, the current-voltage characteristic curve of the OBD with ink-jet silver (black line) shows a sharp increase in the injection current at about 1 V. This indicates the transition of the device from a low conductivity state (OFF state) to a high conductivity state (ON state), and therefore this transition is equivalent to the ''writing'' process in a digital memory cell. The device stays in the ON state as the bias is increased until it reaches another threshold voltage around 7.5 V, indicating the transition of the device from a high conductivity state (ON state) to a low conductivity state (OFF state), and this transition is equivalent to the ''erasing'' process in a digital memory cell. For the comparative device of evaporated silver electrode, the ON-state current density is larger than that of the of ink-jet silver OBD about 2 order, and the turn on and turn off voltage of ink-jet silver OBD is larger than the evaporated silver OBD by 0.2 and 2.7 volt, respectively.

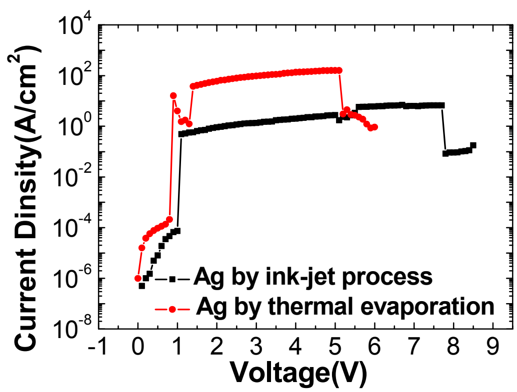


Figure 4. Typical J-V curve of copper-based OBD with different processing used for silver bottom electrode, wherein the black line is the ink-jet printed silver OBD and the red line is the evaporated silver OBD.

The Current-Voltage Characteristics About ON State and OFF State

The current density–voltage (J–V) characteristics of the device with different state are shown in Fig. 5. When the bias is ramped from 0 to 1 V, the initial current injection is very low. When the bias reaches a threshold voltage of approximately 1 V, the device switches from the low conductance (OFF) state to a high conductance (ON) state. When the read voltage is set as 0.5 V, the resulting current density of OFF state and ON state are 8 μA/cm^2 and 0.3 A/cm^2, respectively. The on/off ratio of the conductivities of the two states can reach about 10^5.

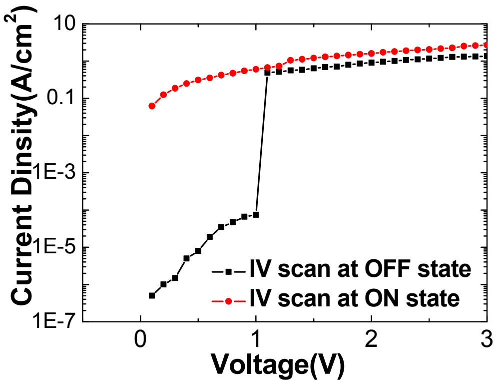


Figure 5. The typical J-V curve of copper-based OBD on different states, in which the black line is OFF state and the red line is the ON state.

Conclusion

In this paper, we have successfully demonstrated an organic bi-stable device fabricated by ink-jet printing bottom silver electrode and thermal evaporating the rest. By modulating the ink-jet printing parameters, a good sintered silver electrode is formed having a line width of about 200μm and an average thickness of about 300nm with moderate roughness. Furthermore, the sheet resistivity of the ink-jet printed electrode can reach about 100~200 mΩ/□, which is low enough to be a good conductor. OBD devices with the structure of ink-jet printed silver electrode/buffer layer/organic layer/buffer layer/copper electrode have been fabricated combining ink-jet and vacuum thermal deposition methods. It has apparent bi-stable state by controlling the Cu-ion (Cu^+) concentration within the organic layer. When the read voltage is set at 0.5V, the ON/OFF ratio is about 10^5. In the future, we expect to make an all ink-jet printed organic bi-stable device with comparable performance to an evaporated or spin-coating counterpart.

References

1. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature* 1999, *397,* 121-128.
2. C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becher, and K. Meerholz, *Nature* 2003, *421,* 829-833.
3. H. Sirringhuas, N. Tessler, and R. H. Friend, *Science* 1998, *280,* 1741-1743.
4. C. D. Dimitrakopoulos and D. J. Mascaro, *IBM J. Res. & Dev*. 2001, *45,* 11-27.
5. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* 1995, *270,* 1789-1791.
6. C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, *Adv. Funct. Mater.* 2001, *11,* 15-26.
7. J. C. Scott, *Science* 2004, *304,* 62-63.
8. Y. Chen, D. A. A. Ohlberg, X. Li, D. R. Stewart, R. S. Williams, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, D. L. Olynick, and E. Anderson, Appl. Phys. Lett. 2003, 82, 1610-1612.
9. L. P. Ma, J. Liu, and Y. Yang, *Appl. Phys. Lett.* 2002, *80,* 2997-2999.
10. L. P. Ma, S. Pyo, J. Ouyang, Q. F. Xu, and Y. Yang, *Appl. Phys. Lett.* 2003, *82,* 1419-1421.
11. L. D. Bonano, B. W. Kean, V. R. Deline, J. R. Salem, and J. C. Scott, *Appl. Phys. Lett.* 2004, *84,* 607-609.
12. J. Ouyang, C. W. Chu, C. R. Szmanda, L. P. Ma, and Y. Yang, *Nature Materials*, 2004, *3,* 918-922.
13. W. D. Brown and J. E. Brewer, Nonvolatile Semiconductor Memory Technology (IEEE, New York, 1998).
14. L. P. Ma, Q. F. Xu, and Y. Yang, *Appl. Phys. Lett.* 2004, *84,* 4908-4910.
15. Stephen F. Pond, "Inkjet Technology and Product Development Strategies", Torrey Pines Research (2000)
16. Kevin Cheng et al, "A Novel Application of Ink-Jet Printing Technology on Manufacturing Color Filter for Liquid Crystal Display", NIP 17: International Conference on Digital Printing Technologies, pp.739-743, 2001.

Author Biography

C. F. Sung received his Master degree in engineering and system Science from National Tsing Hua University in 2003. He is now a process integration & verify engineer in the printing technology division, Opto-Electronics and Systems Laboratories of Industrial Technology Research Institute at Taiwan. His work has primarily focused on the industrial ink-jet printing processes development, especially in PLED (polymer light emitting diodes), OBD(organic bi-stable device) and OTFT device fabrication by ink-jet printing. buttonsong@itri.org.tw