One-Time Programmable Metal-Molecule-Metal Device*

Shang Liwei, Liu Ming†, Tu Deyu, Zhen Lijuan, and Liu Ge

(*Institute of Microelectronics, Chinese Academy of Sciences, Beijing* 100029, *China*)

Abstract: A one-time programmable metal-molecule-metal device, with a modified Rotaxane LB film as the functional layer, is proposed for potential use in organic programmable and fault tolerant circuits like inorganic anti-fuse devices used in field programmable gate arrays. All fabrication methods involved are low temperature processes, ensuring that this device can be integrated with other organic devices. Electrical measurements show that this device has a good one-time programming capability. Its break down voltage is 2.2V, off-state resistance is 15kΩ, and on-state resistance is 54Ω. These characteristics come from the penetration of metal atoms into molecular film under high electronic field.

Key words: molecular device; FPGA; Rotaxane; programmable
PACC: 7340R
CLC number: O484.4^{+}2　　**Document code**: A　　**Article ID**: 0253-4177(2008)10-1928-04

1 Introduction

In recent years, organic semiconductors have made significant progress in electronics applications such as displays, memory arrays, smart cards, and inventory tags[1]. Using organic devices, functional circuits such as inverters, ring oscillators[2], rectifiers[3], frequency dividers[4], differential amplifiers[4], flip-flops[5], and shift registers[6] have been fabricated. Several organic programmable devices have also been developed. Lai *et al*.[7] developed switch devices with stable "read-write-read-erase" cyclic programming characteristics using poly n-vinylcarbazole film. Wu *et al*.[8] developed 30nm crossbar circuits with organic thin film for reprogramming applications. Organic programmable devices are expected to have a huge impact in applications of organic memory, field programmable gate arrays (FPGA), and fault tolerant circuits.

In this paper, we demonstrate the fabrication and characteristics of a one-time programmable metal-molecule-metal device, which can be used for organic memory, FPGA, and fault tolerance designs. This device is a two terminal device with a very high resistance in an un-programmed state and can be programmed by applying a voltage pulse that creates a low resistance link between the two terminals[9]. Using an organic molecular LB film as the functional layer, the device can be completed through low temperature processes, which is necessary to fabricate organic circuits. The characteristics of this device including the breakdown characteristics, on/off-state resistance (R_{on}/R_{off}), and life time are obtained by experiments and analysis. According to the analysis, this device is suitable for constructing organic programmable circuits with low operating voltage organic field effect transistors (OFET) having high-k dielectric materials.

2 Experiment

The bistable Rotaxane synthesis was performed in the key laboratory of the Organic Solid Institute of Chemistry of the Chinese Academy of Sciences, similar to the report in Ref. [10]. Some modifications were performed. In order to enhance the interaction between the tetrathiafulvalene (TTF) unit and the ring component, the -SMe part is removed. Also, the possibility to form LB film is improved by replacing the hydrophobic tetraarylmethane-based stopper by a larger flexible ramiform group. The molecular formula of the modified Rotaxane is shown in Fig. 1. The inset in Fig. 2 shows the configuration of this device. It was fabricated onto a 200nm-thick silicon nitride (SiN_x) film deposited by low pressure chemical vapor deposition (LPCVD) on silicon wafer. First, an 8nm-thick Au bottom electrode with 10nm-thick Cr as an adherent layer was fabricated through photolithography and lift-off processes. Then a Rotaxane monolayer was deposited onto the sample by LB film method. Exposed in the air for a long time, the organic thin-

* Project supported by the National Natural Science Foundation of China (Nos. 60676001, 60676008, 60236010, 60290081) and the State Key Development Program for Basic Research of China (No. 2006CB806204)
† Corresponding author. Email: liuming@ime.ac.cn
Received 7 May 2008, revised manuscript received 21 June 2008

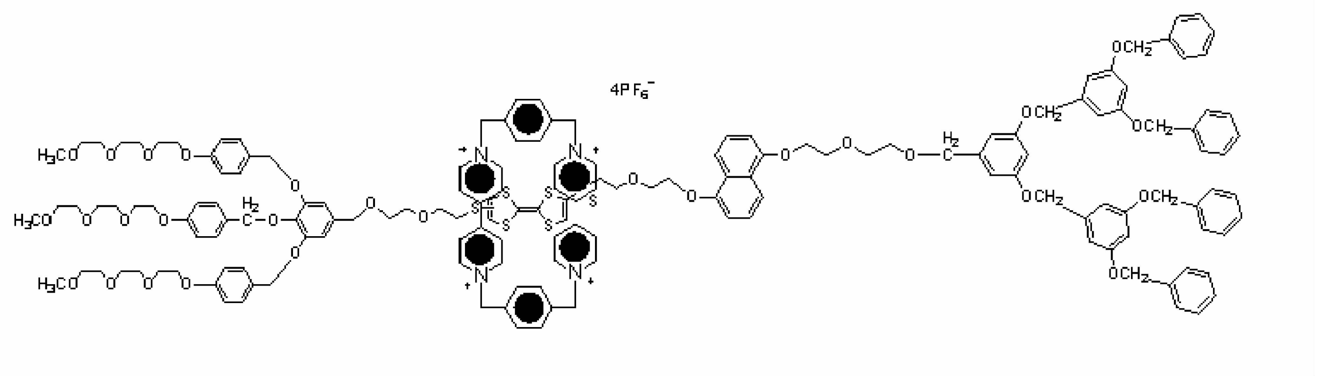

Fig. 1　Modified molecular structure of Rotaxane

film will degrade. So a protective layer of 20nm-thick Ti film was deposited to cover the organic film by electron beam evaporation immediately after the LB process. This Ti film protects the organic film in two aspects: one is to separate the LB film from air; and the other is to prevent the photo-resist and organic solvent in later processes from contacting and damaging the functional thin film. Next, on the protective layer, the top electrodes with 10nm-thick Cr and 80nm-thick Au were fabricated by the same process as the bottom Cr/Au electrode. Finally, the Ti protective layer was etched by inductive coupled plasma (ICP) with CHF_3 and O_2 at the power of 50 and 400W to finish the fabrication. All these treatments above are low temperature (nearly room temperature) processes and are compatible with processes used in organic circuits, such as inkjet printing, spin coating, etc.

3　Results and discussion

The *I-V* characteristics of this device were measured on a Keithley 4200 Semiconductor Characterization System with a CASCADE RF 1 probe station in ambiance at room temperature. Figure 2 shows the

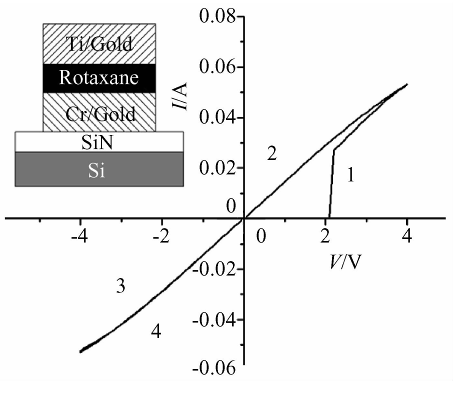

Fig. 2　Typical *I-V* characteristic of a 2μm × 2μm metal-molecule-metal device obtained by applying positive bias voltages to the upper electrode first, following a negative voltage　The inset picture is the schematic cross configuration of this device.

typical *I-V* characteristic of the device. The bias voltage of the top electrode sweeps from zero to a positive value first (curve 1), then it decreases to zero (curve 2) and sweeps to a negative value (curve 3). Finally, it sweeps back to zero (curve 4). We took many measurements. Most of the breakdown voltages (V_{bd}) are about 2.2V. According to the guide rules[11], the programming voltage (V_{pp}) was analyzed to be 2.5V. The off-state resistance (R_{off}) of this device is about 15kΩ. Once programmed, the device becomes an ohmic resistor with a mean resistance of 54Ω. The ratio of on/off current is nearly 3×10^2. After programming, even when a negative voltage was applied, the device remained in the on-state, showing a one-time program capability.

Generally, the Rotaxane film in a crossbar circuit is bistable and can be written and erased many times[12~14] due to its special molecular structure, which has a moveable molecular ring between two supporting molecular groups. That our device is irreversible after programming from off-state to on-state may be because of the removal of the -SMe molecular group, the reaction between the organic molecular film and metal electrode[15], or the penetration of evaporated metal atoms through the organic monolayer[16] when applying the bias voltage to form high conductive links.

In order to make clear which one above is responsible for this conversion, a different device configuration, which has a single layer of gold film (80nm) deposited through a shadow mask as the top electrode and having a symmetrical configuration, has been fabricated. About 20% of the devices show bistable characteristics (Fig. 3 (a)), which demonstrates that our modified Rotaxane LB film is multi-time programmable, i.e., one-time programmable capability is not an intrinsic characteristic of this film. However, the ratios of on/off current of the bistable devices decrease when the number of write-erase cycles increases and change to 1 finally, so these bistable de-

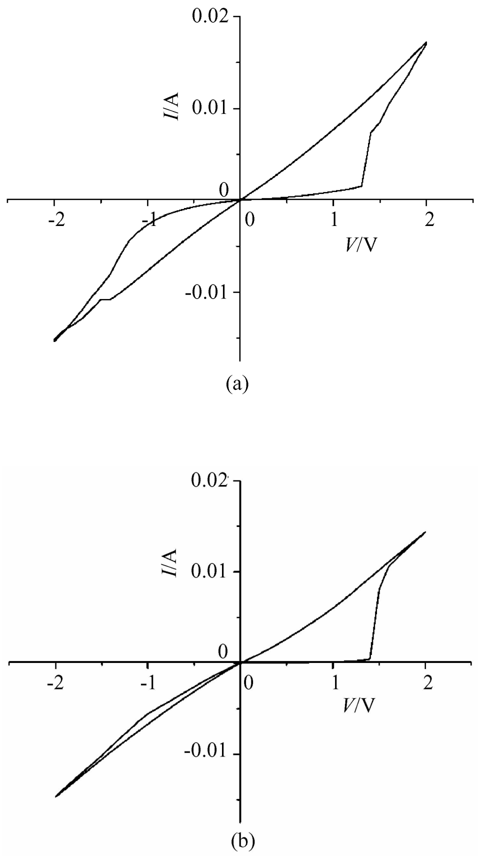

Fig.3 Typical I-V characteristic of a 2μm×2μm metal-molecule-metal device with a top electrode of single layer gold film (a) Multi-time programmable characteristic;(b) One-time programmable characteristic The positive V_{bd} of both is 1.4V.

vices will not harm the application of our device as a large scale array. A great number of these devices show a one-time programmable characteristic (Fig. 3 (b)). The V_{bd} of both one-time and multi-time programmable devices are 1.4V, or 0.8V lower than that of the asymmetrical configuration. Due to the extra thin Rotaxane film (2~3nm), applying a small voltage (1~2V) will produce a tremendous electronic field (10MV/cm) between the two metal electrodes. This extra high field gives the metal atoms energy high enough to penetrate the film, leading to a one-time program characteristic of the device.

Figure 4 shows a tight distribution histogram of the on-state resistance, R_{on}. The mean value of R_{on} is 54Ω, which demonstrates that a high conductivity link is formed in the programmable device and the parasitic resistance associated with the electrode resistance is very low. Thus, this one-time programmable device has a great advantage as an interconnect device[17].

One important task in determining the feasibility of programming devices is to examine their life time. Typical electrical field accelerated tests were carried out in order to study this performance under normal operating conditions. Figure 5 shows the plot of life-

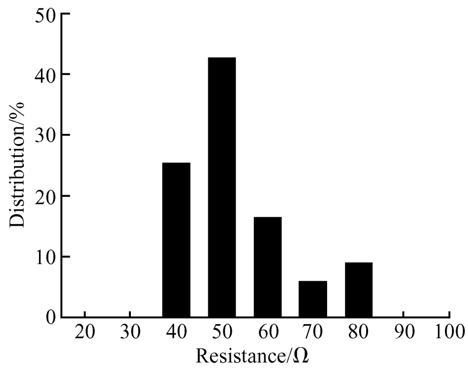

Fig.4 Histogram of on-state resistances for 2μm×2μm metal-molecule-metal device programmed with voltage pulses of 2.5V Programming pulses were applied to the upper electrodes.

time as a function of reciprocal of bias voltage. Time to breakdown (T_{bd}) of the device operating at 1.5V is extrapolated to be more than 10^9s. This T_{bd} can be improved by increasing the thickness of the organic layer.

Typical applications of this one-time programmable device are organic programmable circuits, such as FPGA and fault tolerant circuits in which it is used as an interconnect device and organic transistors[18,19] as logic components. Using high-k $SrBi_2Ta_2O_9$ films as a gate insulator and pentacene as a semiconductor, Han *et al*.[18] have fabricated OFET with a very low working voltage (4V) and threshold voltage (0.64V). Choi *et al*.[19] have also demonstrated an OFET with a low operating voltage (2.5V) and threshold voltage (0.1V) using high-k $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ film as the dielectric and pentacene as an active layer. These voltages can be further reduced by decreasing thickness or increasing the dielectric constant of insulating films. Thus, this metal-molecule-metal device can be efficiently integrated with these low operating voltage organic transistors due to their similar fabrication processes, and can provide programmable capabilities to the organic circuits, which are essential for programmable and fault tolerance applications.

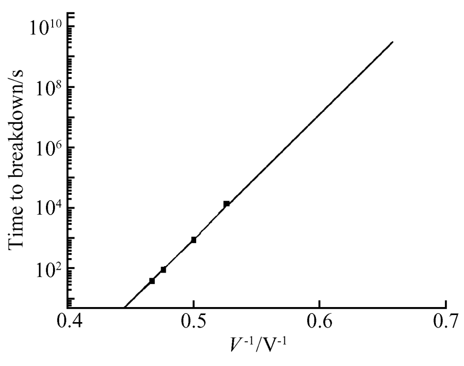

Fig.5 Time breakdown plot of the metal-molecule-metal device

4 Conclusion

In this paper, a one-time programmable metal-molecule-metal device was fabricated through low temperature processes and characterized. This device has a break down voltage of 2.2V, leading to a programming voltage of 2.5V. It has an off-state resistance of 15kΩ and a mean on-state resistance of 54Ω. The life-time is more than 10^9s under programmable voltage. Integration with this device as the programmable interconnect device and low operating voltage organic transistors as logic components will make many future organic programmable circuits such as FPGAs, and fault tolerant circuit, into application.

Acknowledgemets The authors would like to thank Mr. Liu Yunqi and Qiu Wenfeng for organic material synthesis.

References

[1] Klauk H, Gundlach D J, Jackson T N. Fast organic thin-film transistor circuits. IEEE Electron Device Lett, 1999, 20: 289
[2] Fix W, Ullmann A, Clemens W. Fast polymer integrated circuits. Appl Phys Lett, 2002, 81: 1735
[3] SteudelL S, Myny K, Arkhipov V, et al. 50MHz rectifier based on an organic diode. Nat Mater, 2005, 4: 597
[4] Kane M G, Campi J, Hammond M S, et al. analog and digital circuits using organic thin-film transistors on polyester substrates. IEEE Electron Device Lett, 2000, 21: 534
[5] Crone B, Dodabalapur A, Lin Y Y, et al. Large-scale complementary integrated circuits based on organic transistors. Nature, 2000, 403: 521
[6] Crone B K, Dodabalapur A, Sarpeshkar R, et al. Design and fabrication of organic complementary circuits. J Appl Phys, 2001, 89: 5125
[7] Lai Y S, Tu C H, Kwong D L, et al. Bistable resistance switching of poly (N-vinylcarbazole) films for nonvolatile memory applications. Appl Phys Lett, 2005, 87: 122101
[8] Wu W, Jung G Y, Olynick D L, et al. One-kilobit cross-bar molecular memory circuits at 30-nm half-pitch fabricated by nanoimprint lithography. Appl Phys A, 2005, 80: 1173
[9] Liu S, Lamp D, Gangopadhyay S, et al. A new metal-to-metal antifuse with amorphous carbon. IEEE Electron Device Lett, 1998, 19: 317
[10] Lee I C, Frank C W, Yamamoto T, et al. Langmuir and Langmuir-Blodgett films of amphiphilic bistable rotaxanes. Langmuir, 2004, 20: 5809
[11] Takagi M T, Yoshii I, Ikeda N, et al. A highly reliable metal-to-metal antifuse for high-speed field programmable gate arrays. International Electron Devices Meeting, 1993: 31
[12] Stewart D R, Ohlberg D A A, Beck P A, et al. Molecule-independent electrical switching in Pt/organic monolayer/Ti devices. Nano Lett, 2004, 4: 133
[13] Luo Y P, Collier C, Jeppesen J O, et al. Two-dimensional molecular electronics circuits. Chem Phys Chem, 2002, 3: 519
[14] Deng W Q, Muller R P, Goddard III W A. Mechanism of the stoddart-heath bistable rotaxane molecular switch. J Am Chem Soc, 2004, 126: 13562
[15] Chang S C, Li Z Y, Lau C N, et al. Investigation of a model molecular-electronic rectifier with an evaporated Ti-metal top contact. Appl Phys Lett, 2003, 83: 3198
[16] Jung D R, Czanderna A W, Herdt G C. Interactions and penetration at metal/self-assembled organic monolayer interfaces. J Vac Sci Technol A, 1996, 14: 1779
[17] Abea T G, Sturm J C. Programmable organic thin-film devices with extremely high current densities. Appl Phys Lett, 2005, 87: 133502
[18] Han S, Liu X, Han J P, et al. Polymer thin-film transistors with high dielectric constant gate insulators. Appl Phys A, 2003, 77: 873
[19] Choi Y W, Kim D, Tuller H L, et al. Low-voltage organic transistors and depletion-load inverters with high-*k* pyrochlore BZN gate dielectric on polymer substrate. IEEE Trans Electron Devices, 2005, 52: 2819

单次可编程金属-分子-金属器件*

商立伟 刘 明† 涂德钰 甄丽娟 刘 舸

（中国科学院微电子研究所，北京 100029）

摘要：提出了一种单次可编程的金属-分子-金属器件.该器件利用一种经过改良的 Rotaxane LB 膜作为功能层，可以和应用于场编程门阵列电路中的无机反熔丝器件相比拟，将在有机可编程电路和容错电路等方面有较广泛的应用.所有的加工工艺都是低温工艺，使得该器件可以和其他有机器件集成.电学测试表明该器件有良好的单次编程能力，其击穿电压为 2.2V，关态电阻为 15kΩ，而开态电阻为 54Ω.据分析，这一特性是由非对称的电极结构和金属原子在高电场作用下穿透了分子薄膜所造成的.

关键词：分子器件；场编程门阵列；Rotaxane；可编程
PACC：7340R
中图分类号：O484.4+2 **文献标识码：**A **文章编号：**0253-4177(2008)10-1928-04

* 国家自然科学基金(批准号:60676001,60676008,60236010,60290081)和国家重点基础研究发展规划(批准号:2006CB806204)资助项目
† 通信作者.Email:liuming@ime.ac.cn
2008-05-07 收到,2008-06-21 定稿