Organic Electronics 53 (2018) 83–87

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Field-dependent, organics assistant filamentary mechanism in both vertical and planar organic memories

Qi Zeng[a,*], Jiajun Qin[a], Xiaoqing Chen[b], Xiaoyuan Hou[a,**]

[a] State Key Laboratory of Surface Physics, Key Laboratory of Micro and Nano Photonic Structures (Ministry of Education), Collaborative Innovation Center of Advanced Microstructures, Fudan University, Shanghai 200433, China

[b] Global Research Center for Environment and Energy Based on Nanomaterials Science (GREEN), National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

ARTICLE INFO

Keywords:
Memory
Filament
NDR
FIB
Nano-fabrication

ABSTRACT

The forming/destruction mechanism of conducting filament is essential in understanding the behavior of resistance-memory device. On the basis of filamentary theory, we systematically studied the different electrical performances of both planar and vertical sandwich (metal/organic/metal) memory devices. Bias induced morphological change in gap devices are monitored using scanning electron microscopy system equipped with probes. The in situ images directly demonstrate that with bias increasing, metal clusters emerge inside the channel and further cause sudden switching of device resistance. After clarifying the roles of electrodes and sandwiched organic layer, we conclude a field-dependent filament formation and organics-assistant filament destruction mechanism for resistance memory phenomenon, which should generally exist in all organic electronic devices with metal electrodes.

1. Introduction

The formation/destruction of conductive filament is argued to be the mechanism of many types of organic electric resistance memory devices [1–4]. The formation and destruction of the filaments are reported to be dominated by: 1) atmosphere [5] 2) electrochemical reaction between two electrodes which requires chemical-active media [3,6] and 3) evolution of the metal electrode under bias which should generally exist in all sandwich-structured devices [7,8]. In previous studies on metal-insulator-metal (MIM) resistance-bistable memory devices where various organic small molecular materials [9–12] or polymers [13,14] are used as the insulator layer, similar memory phenomenon is shared. Such common behavior disregarding the insulator material highlights the role of the metal electrode itself. However, what the origin of filaments is and how they are formed, still remain controversial. The most important related feature is that the distribution of the filament is localized [1,15], which means the switching of the resistance takes place only in some specific regions of the cell rather than the whole body. Generally the effective filament dimension is tens to hundreds of nanometers [16]. Therefore devices of planar structures by micro/nano-fabrication (e.g. Electron Beam Lithography (EBL), Focus Ion Beam (FIB)) are preferred for studying the kinetics of filament -formation/dissolution in the MIM structure memories [4,17–19], since it enables directly observing the evolution of metal/organic interface without damaging the working devices. For example in planar structure of Ag/polystyrene/Ag device with gap as small as 36 nm, Mutiso reproduced reversible resistance switching characteristics which is the same as observed in traditional vertical sandwich-structured resistance memory devices [18]. In Ag/PEDOT:PSS/Pt device, Gao reported an interesting phenomenon that the Ag clusters, which are first generated at the middle of the organics under low bias and then extend to the two electrodes under high bias, are the conducting filaments that are responsible for the resistance-switching [4]. Krishnan had systematically studied the atomic switching behavior of the Ag-salt incorporated polyethylene oxide (Ag–PEO) devices, which revealed that filament growth behavior strongly depends on the device configuration and experimental parameter such as gap width and the applied compliance current [20].

In this work, with merit of nanofabrication via FIB technique and SEM equipped with electric probes as shown by Fig. 1(a), we are able to directly in-situ monitor the electrodes morphology together with the resistance-switching progress. Starting from electrical characteristics of planar organic memories with a structure of Al/tris-(8-hydroxyquinoline) aluminum (Alq3)/Al, we confirmed the planar device, which allows direct observation of the electrode morphology, is a comparable system to unveil the physics in the conventional vertical devices. By

* Corresponding author.
** Corresponding author.
E-mail addresses: 09110190011@fudan.edu.cn (Q. Zeng), xyhou@fudan.edu.cn (X. Hou).

https://doi.org/10.1016/j.orgel.2017.11.004
Received 28 August 2017; Received in revised form 3 October 2017; Accepted 2 November 2017
Available online 03 November 2017

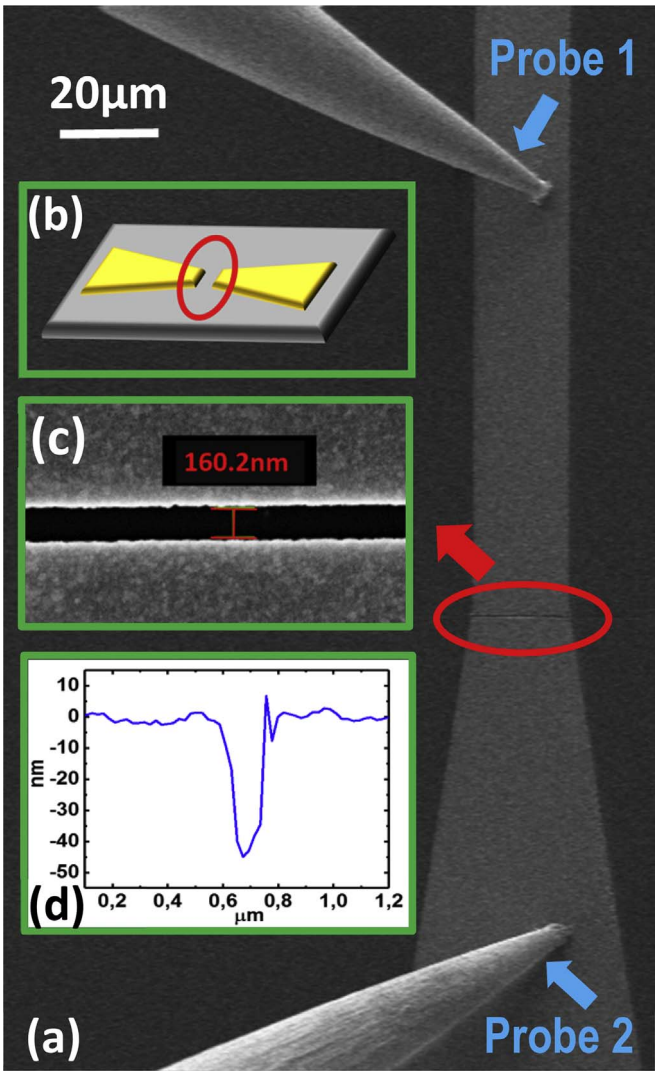

Fig. 1. (a) SEM image of the gap device connected to two probes. (b) A schematic of a gap device. (c) Magnified detail of a gap with a width of 160 nm. (d) AFM result of the depth of the gap.

comparing the I-V characteristics of planar and vertical devices, we propose that the 'switching on' of MIM organic memories origins from the migration of metal atom between two electrodes while the negative differential resistance (NDR) behavior requires the participation of organics. Next, by studying unique 'gap device', a lateral structure comprising two parallel metal electrodes on the substrates separated by a nanoscale gap, in which all molecules are chemical inactive, we proved that the conducting filaments are the roughened electrode surface and migrated ions/atoms by the applied bias.

2. Experiments

As introduced, we start from the comparative study of metal/Alq3/metal devices between conventional vertical structure and planar one. Here Alq3 is chosen as the organic layer because of its reported stable non-volatile memory feature and large on-off ratio in the conventional structure [21,22]. Intrinsic Si wafers are chosen as substrates for nanofabricated devices. The wafers are pretreated by removing the silicon oxide via dipping into the hydrofluoric acid and consequent ultrasonic cleaning in ethanol and deionized water. After sandclock-like metal (Au, Ag, Al) pattern on the substrate is fabricated by ultraviolet lithography, the final gap device is obtained by dividing the pattern into two halves using FIB etching (FIB-SEM crossbeam, Zeiss), as illustrated in Fig. 1(b). The width of these gaps is 70–200 nm, which is of the same scale as the vertical ones in our work. Finally, the planar device is completed by filling the Al gap device with thermally deposited Alq3. A conventional vertical device with same functional structure of Al/Alq3/Al is prepared as a reference according to our previous fabrication procedure [15,23]: Commercial patterned Indium tin oxide (ITO) glass with sheet resistance of 17Ω/square are used as substrate. Each one is solvent-cleaned in an ultrasonic system and dried before transferred into a high vacuum chamber for the following deposition of 5 nm Al, then Alq3 and Al electrode, in which the first Al layer on ITO acts as the anode to form a symmetrical device. The measurements of electric properties of both planar and vertical devices are carried out in a nitrogen glove box (O_2 < 1 ppm and H_2O < 1 ppm). All above procedure are operated in a 100-class cleanroom to avoid contamination.

In order to exclude the electrochemical reaction between two electrodes and the impact of the organics medium, gap devices are designed with electrodes of same metal materials but without Alq3 materials inside. For further study of behavior of the electrode atoms under electric field, we observe the morphology of the gap device under bias by employing SEM-system with conductive probes. As SEM image of Fig. 1(a), bias is applied between two electrodes of the gap structure. This setup make it possible to monitor the in-situ morphology while the electrical measurement is proceeding, using an external Keithley 2400 sourcemeter. Gap-devices of different widths and metal materials are tested.

3. Results and discussion

Fig. 2(a) is the performance of a planar Al-Alq3-Al device. The deposition thickness of Alq3 is 50 nm. The width of the planar structure used is 100 nm, comparable to the layer thickness of typical vertical device. The I-V curve indicates a remarkable switching phenomenon with on/off ratio of 10^4. In the first scanning from 0 to 20 V, the device switches on from high resistance state (HRS) at the threshold voltage of 10 V and keep at the low resistance state (LRS) during the reverse scanning from 20 to 0 V. After that the LRS of planar device cannot be erased by either positive or negative bias, exhibits a 'write once read many' (WORM) like memory mode. While I-V characteristics of vertical device is shown in Fig. 2(b), current switch on abruptly at the threshold voltage V_{th} of 3 V at first scanning from 0 to 10 V and after achieving a maximum V_{max} it began to decrease, showing NDR effect. Then in the following reverse scanning it stays at LRS. However, the memory behavior of vertical one is rewritable since this LRS can be erased by a voltage larger than V_{max} and recovered by a voltage below the V_{th}, as reported before [15]. What's more, the memory also works in the negative bias region because of the symmetrical I-V curve.

The results indicate that threshold switching phenomenon also exist in planar device of micrometer-scale. Furthermore, two obvious differences are found when comparing the I-V curves of planar structure with the vertical one.

First, the threshold voltage of the vertical device is lower than planar one, which is attributed to the rougher Al/Alq3 interface in vertical device caused by metal atoms penetration into the organic layer during deposition of the top electrode. According to the field-induced filament evolution model [23,24], conducting filaments can form when local electric field is high enough for electron/ion emission, which further switch on the device. Meanwhile, under a certain bias, the rougher interface with sharper metal protrusions towards the organic bulk, can result in a much higher localized electric field than a flat surface [7]. Therefore the formation of filaments in vertical device are much easier than in planar one.

The next difference is that memory behavior in vertical structure is rewritable resistance memory with NDR phenomenon while in planar one is WORM-like. This should be related to the special structure of planar device, which have particular surface exposed to air and interfaces with substrates. Gao have reported that conducting path in the