Impact of electroforming polarity on TiO_2 based memristor

Jinling Xing, Qingjiang Li, Sen Liu, Haijun Liu, and Hui Xu^{a)}

College of Electronic Science and Engineering, National University of Defense Technology, Changsha, 410073, China

a) xuhui@nudt.edu.cn

Abstract: The impact of electroforming polarity on solid $Pt/TiO_2/Pt$ memristor is studied. We observe the negative electroforming leads to small and concentrated forming voltages; while positive electroforming leads to the relatively larger and dispersed forming voltages. These phenomena are interpreted by employing a modified bipolar percolation model. We argue the distribution of polarity-related forming voltage is attributed to the different filament growth patterns under the different electroforming polarities. This work facilitates understanding the electroforming procedure and then benefits fabrication for reliable devices with controllable electroforming behaviour.

Keywords: memristor, electroforming, polarity, percolation model

Classification: Electron devices, circuits and modules

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1 Introduction

Recently, interest in a considerably downscaled nano-electronic ReRAM device (memristor [1]) has been remarkably increasing due to its intrinsic capabilities of executing multiple applications ranging from non-volatile information storage [2] to reconfigurable circuits [3], logic [4] and neuromorphic computing [5].

The scaling promise hinges on the compact device arrangement in crossbar array, whereby sets of mutually perpendicular word-line and bit-line electrodes sandwiching the transition material of a device at each joint. The memory integration density of the lateral crossbar can reach $4F^2$ [6] where F is the minimum feature size. However, the practical applications of memristors crossbar may be hindered by the electroforming procedure; a random and uncontrollable electrical pretreatment before the device achieves stable resistive switching [7]. The one-time, irreversible procedure is generally implemented by building extensively high electric field inside the material to generate massive defects [8, 9]. As a wide range of device properties are dependent on the details of the electroforming, it is necessary to explore methods to mitigate the divergence of electroforming parameters (i.e. forming voltage, formed resistance) to achieve electroformed devices with relatively uniform performances. Yang *et al.* [10] found reducing the active metal oxide thickness was an effective way to eliminate the electroforming procedure. Lee *et al.* [11] adopted the defect tuning engineering through nanocafold films to

create oxygen vacancy channels along the vertical heterointerfaces and thus created electroforming-free memristors devices. However, the working current will increase after the thickness of the metal oxide is reduced, which then increases the power consumption and does not match the future energy-efficient development trend.

Regarding the TiO_2 -based memristors, the rupture and formation processes of conductive filaments consisting of oxygen vacancy is widely seen as the key factor for resistive switching [8, 9]. The electroforming process is regarded to be implemented by the drift of oxygen vacancy from the anode to the cathode [9]. In our fabricated TiO_2 -based memristors, we find the relatively uniform electroforming parameters can be obtained in a simple way without reducing the oxide thickness. That is implemented by controlling the initial oxygen vacancy distribution during the fabrication and the voltage stimulus polarity during the electroforming process. Specifically, the abundant oxygen vacancy region appears near the top electrode area during fabrication, then the proper polarity of the sweep voltage stimulus is applied on the devices. We find the distributions of forming voltage are significantly different for positive electroforming and negative electroforming cases. Positive electroforming leads to large and dispersed forming voltages, while negative electroforming brings relatively small and concentrated forming voltages. This phenomenon is then interpreted by a modified bipolar percolation model. Simulation results show a good agreement with the experiment data and then in turn demonstrate the feasibility and validity of the model. Therefore, we speculate that the difference of forming voltage can be attributed to the different growth pattern of filaments under the different electroforming polarities.

2 Methods

2.1 Device fabrication

Fig. 1. SEM images for TiO_2 based prototype device. (a) Sketch image of prototype device with active area of $5\ \mu\text{m} \times 5\ \mu\text{m}$. (b) Image of the cross section of the active core. Each layer thickness is shown inside the image.

The devices under test (DUT) possess the vertical structure of $\text{Si}/\text{SiO}_2/\text{Ti}/\text{Pt}/\text{TiO}_2/\text{Pt}$ seen from bottom to top. The fabrication procedures are described as follows. First, 100 nm thickness of SiO_2 was thermally grown on a 2-inch Si wafer to serve as the insulating layer, followed by 5 nm Ti layer and 30 nm Pt layer where Pt acted as bottom electrode (BE) and Ti was used to enhance adhesiveness for Pt layer. Both Ti and Pt (BE) were deposited by the E-beam evaporation technique. 15 nm

active layer TiO_2 was then deposited by atomic layer deposition technique. At last, the 50 nm TE Pt was prepared as the top electrode (TE) by RF magnetron sputtering technique above TiO_2 layer. Both TE and BE were patterned by the optical lithography and standard lift-off process. All DUTs had active area of $5 \times 5 \mu m^2$. The SEM images of a 1×1 cross-point device and the cross section of active core were displayed in Fig. 1.

2.2 Electrical measurements

All quasi-DC I - V curves of devices were obtained by Keithley semiconductor characterization system 4200SCS. During the measurement, TE was voltage sourced while maintaining BE grounded. The prototype device was electrically probed on wafer to Keithley 4200SCS via the Cascade Summit 11000 semi-automated probe station. The quasi-DC I - V relation was investigated by two SMU modules where one module was configured into the voltage sweep mode and another was into the zero-biased mode. The pulsing performance of the electroformed devices were assessed by the self-developed ReRAM characterization instrument [12].

3 Results and discussion

Fig. 2. Pristine and electroforming I - V curves (a) Pristine I - V curve. Inset: measured data and fitting result by Schottky emission model at $-1 \sim -3$ V. (b) Electroforming I - V curves. One color stands for one device which is formed in either positive voltage sweep or negative voltage sweep. During the forming procedure, the compliance current (CC) is set to 70 μA .

Fig. 2(a) shows the typical I - V curve of one pristine device obtained by applying the voltage sweep from +3 V to -3 V in step of 0.05 V. It is clear that the device exhibits the asymmetric diode-like I - V relation. By fitting data of the negative voltage region with Schottky emission model where the plot of $\ln(I)$ versus $V^{0.5}$ is linear [13], a well matched result is obtained, which indicates that the high work-function BE Pt(5.65 eV) and TiO_2 forms a Schottky diode. Besides, the series connection of one resistor and one diode is reported to generate the similar I - V curve [14]. As the metal/semiconductor interface is typically rectifying in the case of low doping and ohmic for heavy doping [10], it is reasonable to deduce that the dopant density of oxygen vacancy at TiO_2 /Pt(BE) interface is lower than that in other TiO_2 film area.

Fig. 3. Measured and simulated forming voltage statistical characteristics. Each measured data corresponds to one device. The simulation parameters set-up: defect density $p_{top} = 0.3$, $p_{film} = 0.2$, $p_{bottom} = 0.02$ for film top interface region, bulk film region and bottom interface region, respectively; $V_s^{film} = 0.3$, $V_{sp}^{it} = 0.15$, $V_{sn}^{it} = 0.4$, $V_{sp}^{ib} = 0.8$, $V_{sn}^{ib} = 0.15$; $r_H^{film} = r_H^{it} = r_H^{ib} = 2000$, $r_L^{film} = r_L^{ib} = r_L^{it} = 20$. The CC is set to 8 mA.

From Fig. 2(a), we observe that the current flowing through the pristine device is very low even under the large bias voltage ($-0.6 \mu A @ -3 V$), implying a low carrier density exists. That low defect density cannot trigger the stable resistive switching in our devices. In this scenario, an electroforming step is required to introduce massive defects inside the switching film and finally create nanoscale conductive filaments [9]. By setting the CC of 70 μA to protect devices from hard breakdown, we apply a voltage sweep with the absolute amplitude increasing from 0 V to 10 V in steps of 0.05 V on the pristine devices. The sweep would exit once the device current hits the pre-set limit. A total of six different devices are electroformed by each voltage polarity with results depicted in Fig. 2(b). The forming voltage is defined as the point where the abrupt current is induced. Interestingly, the negative forming voltage is concentrated around 4 V, whereas the positive forming voltage disperses into a larger voltage range from 4 V to 10 V. For the purpose of exploring whether the trend exists when more samples are considered, we electroform another 40 devices where each polarity is assigned with 20 devices. The results are illustrated in Fig. 3. We find that the distribution of forming voltage is polarity-related. The positive forming voltage is ranging from 4.4 V~9.3 V, while the negative forming voltage lies in range of $-3.6 V \sim -4.3 V$ with the maximum difference of 0.9 V, much smaller than the difference of 4.9 V for positive forming. Furthermore, the standard deviation of negative forming voltages is 0.21, only one seventh of the positive forming voltages (1.5).

The switching performances of devices after electroforming procedures are depicted in Fig. 4. The bipolar quasi-DC I-V characteristics were attained via the voltage sweeping cycle of $0 \sim 2 V \sim -2 V \sim 0$ in steps of 20 mV with results shown in Fig. 4(a) and Fig. 4(b). In the case of the positive electroforming, the device exhibits the anti-clockwise switching direction where the positive stimulus switches the device from high resistive state (HRS) to low resistive state (LRS). In comparison, the negative electroforming device exhibits a reverse switching trend. The different switching direction indicates that there may exist the different switching regions

Fig. 4. Device switching performance after positive or negative electroforming. (a)(b) Typical I-V curve for positive and negative electroforming, respectively. (c) Pulse performance of the devices electroformed by positive voltage stimulus. Up panel: resistance state change under pulsing. Down panel: corresponding pulse stimulus. (d) Pulse performance of the devices electroformed by negative voltage stimulus.

inside the TiO_2 film after different electroforming procedures. In addition, the pulse performances of devices are shown in Fig. 4(c) and Fig. 4(d). With regard to devices processed by either positive or negative electroforming, repeatedly gradual switching can be attained by administering multiple, fixed-duration (100 μ s)/increasing-amplitude voltage pulse ramps of alternating polarities. Notably, the same switching trend revealed in quasi-DC I-V curves is observed.

It is generally recognized that the electroforming step is accompanied with the generation of oxygen vacancy and reduction reactions from TiO_2 to TiO_{2-x} [9]. Due to the interaction between metal electrode and metal oxide dielectric, that processes might be different between the interface and interior area of oxide film. Accordingly, we speculate the polarity-related forming voltage difference relies on interface effect and initial defects distribution difference between film bulk layer and interface layer.

Here we verify our assumption by employing a modified percolation model. In this model, the TiO_2 dielectric layer is equivalent to the combination of two-dimensional $M \times N$ resistor bond network where each bond possesses two metastable state: low state r_l and high state r_h [15]. The states can be reversely switched between each other depending on the voltage across it. The sketch of the model is displayed in Fig. 5. Inspired by the phenomenological model in Ref. [16], the resistor bond lattice is further divided into three domains: top interface region, film bulk region and the bottom interface region. In film bulk region, each resistor bond has two metastable state, r_l^{bulk} and r_h^{bulk} , marked in black and grey color, respectively. The switching from r_h^{bulk} to r_l^{bulk} is non-polarized and depends on the absolute voltage amplitude across the bond, which is the same with Ref. [17]. Each bond in the top and bottom interface regions has two value, r_h^{int} and r_l^{int} ,

Fig. 5. Sketch of modified percolation model. The active layer is divided into film layer and two interface layers. The switching rules for both layer are shown in the right area.

marked in blue and red color, respectively. The change from r_h^{int} to r_l^{int} is polarity-dependent. Specially, for the bottom interface region, the positive SET voltage V_{sp}^{ib} is larger than negative SET voltage V_{sn}^{ib} , while the negative SET voltage V_{sn}^{it} outweighs the positive SET voltage V_{sp}^{it} for the top interface region. Here, the SET voltage is defined as the threshold voltage above which resistor bond changes its state from high to low. The electroforming simulation is implemented by the collaboration of Matlab 2013b and LTspice V4.22 where Matlab writes circuit network scripts and then calls LTspice to calculate node voltage and bond current.

Specifically, we divide TiO_2 layer into 50×20 resistor bond matrix where 30×20 bonds are assigned to the bulk region and 10×20 bonds for each interface region. The model parameter of the defect density p is set to decrease from the top interface region to bottom interface region in order to be consistent with the results deduced from the pristine I-V curve. Besides, the defects in all regions obey the uniformly random distribution. By repeating the electroforming simulation for 20 times on each polarity, we obtain the results shown in Fig. 3 where the model parameters are listed in the caption area. A good fit result between the simulation and real data in both the amplitude and distribution for both polarity is visible. Our simulation demonstrates that the distribution difference of polarity-relation forming voltage could be described by the modified percolation model.

In order to obtain further insights into the polarity-related forming process, several snapshots during the forming procedure are illustrated in Fig. 6. The panel (a)(b)(c)(d) are associated with the positive forming, while panel (e)(f)(g)(h) belong to the negative forming. An abrupt current jump appears in panel (d) and (h) when the external stimulus reaches the forming voltage, which is in accordance with the experimental results in Fig. 2. For the positive forming, we observe that the filament grows from the top interface region, ending in the bottom interface region. Reversely, in the case of the negative forming, the filament firstly grows from the bottom interface region and ends in the top interface region. Generally, a conclusion stands that the larger defect density usually leads to narrower forming voltages because of larger possibilities to generate the ‘preferable conduction path’

Fig. 6. Snapshots during the electroforming procedure simulation. The simulation parameters are the same with the Fig. 3. The value shown above each panel stands for the voltage of external stimulus.

where the filament will be triggered to grow. Under the simple switching rule for the proposed model, the relatively larger positive forming voltage variation is induced by the low defect density near the bottom electrode interface, while the negative electroforming with more concentrated forming voltages is benefited from the comparatively larger defect density in the film bulk layer and top interface region.

In terms of the simulation results in Fig. 6, the complete filament penetrating across the film is formed for the large CC setting of 8 mA, while the smaller CC setting (i.e. under 5 mA) will result in incomplete filament. In specific, the incomplete section is located in the bottom interface region during the positive electroforming simulation. Reversely, the negative electroforming results in the incomplete section in the top interface region. The simulation results can interpret the switching behaviour of devices after electroforming process. With the small CC of 70 μ A in the experiments, the incomplete filament is formed and the non-linear I-V relation is induced. As a result, the switching region sites at the tunnelling gap between the electrode and the tip of the longest incomplete filament [18]. With regard to devices after positive electroforming, the gap stands near the bottom electrode. Consequently, the positive stimulus drives the oxygen vacancy towards the bottom electrode. As a result, the gap is reduced and the device resistance decreases. In comparison, the negative forming process results in a gap near the top electrode. In this case, the positive stimulus pushes the oxygen vacancy away from the top electrode and broadens the gap, resulting in the resistance increase.

Moreover, the proposed model can provide some interesting predications for device fabrication optimization. By only increasing the initial defect density p_{int} in the interface region and keeping all other simulation parameters the same with the Fig. 3, 20 times of positive forming procedures are performed for each p_{int} . Consequently, the mean and the standard deviation value of positive forming

Fig. 7. Positive forming voltage statistics as a function of initial interface region defect density. Other simulation parameters are the same with the Fig. 3.

voltage are obtained shown in Fig. 7. Results shows the standard deviation reduces significantly from about 0.93 to 0.53 when the p_{int} increases from 1% to 9%. Meanwhile, the corresponding mean value reduces by 1.88 V. That means uniform forming behaviour can possibly be achieved by simply controlling the initial defect density inside the switching material.

4 Conclusion

In summary, we mainly focus on understanding the electroforming polarity effect on forming voltage statistics in solid-state TiO_2 based memristor. We find negative electroforming leads to small and concentrated forming voltages, while positive electroforming results in relatively larger and dispersed forming voltages. The phenomenon is attributed to different filament growth pattern originating from the initial defect density difference between bulk layer and interface layer of TiO_2 film. A modified percolation model is proposed to interpret the experiment results. We argue the positive forming voltage statistics is dominated by the defect density in the bottom interface region, whereas the negative forming voltage distribution is governed by the TiO_2 bulk region. The work provides an alternative view to understand the polarity dependent electroforming behaviour and a possible way to achieve uniform device performances in large-scale ReRAM devices applications by controlling electroforming process with the defect distribution engineering.

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