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Unidirectional Threshold Switching Induced by Cu Migration with High Selectivity and Ultralow OFF Current Under Gradual Electroforming Treatment

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ABSTRACT

Gradual electroforming process was implemented on pristine Pt/HfO_x/Cu/Pt structure to realize volatile threshold switching characteristics of a diffusive memristor. The reported devices exhibit stable unidirectional threshold switching properties with high selectivity of $>10^7$ and ultralow OFF current of ~ 100 fA for over 10^4 endurance cycles. Nucleation theory on spheroidal-shaped metallic filament growth is used to extensively discuss the structural changes of the device after gradual forming treatments by analysing the applied bias amplitude dependency of the finite delay time required by the device to turn ON under external electric field. On the other hand, Rayleigh instability model was implemented for the aforementioned spheroidal metallic nucleus to explain the relaxation dynamics of the device. It was shown that the relaxation time of the device depends on the initial profile of the nucleus within the insulating layer. The broadening of ON current distribution of the device was observed during the device endurance test. This is correlated to the presence of random telegraph signal (RTS) during the ON state of the device.

Introduction

Memristive devices are promising non-volatile memory technologies due to its high scalability, high-speed operation, low power consumption, and multibit per cell capability. These desirable characteristics are required for both embedded and standalone mass storage devices. Recently, the artificial intelligence technology, which utilises new high-level computing approach, has been on a quest in search of ideal synaptic devices to realize a highly dense computing platform, which requires high synaptic weight precision. Thus, the high scalability nature and multibit per cell capability demonstrated in many memristive devices have attracted a great deal of attention from the neuromorphic computing community to fulfil their ideal synaptic device requirements.

In order to fully utilise the scalability of a memristive device through highly connected crossbar array, a select device or selector is required to work in tandem with the memory element to mitigate the inherent sneak path current issue of the architecture. In the recent years, different types of selectors have been widely investigated. These selectors can be classified into two major categories, *i.e.* non-linear IV and threshold IV selector. Non-linear IV selector are those devices implementing metal-oxide Schottky barrier modulation,¹⁻⁷ crested and variable oxide tunnel barrier,⁸⁻¹³ and mixed of ionic electronic conductors (MIEC).¹⁴⁻¹⁷ On the other hand, the threshold IV selector consists of ovonic threshold switch (OTS),¹⁸⁻²⁰ metal-insulator transition (MIT),²¹⁻²⁴ and diffusive memristor (DM).^{7, 25-45} Among these select devices, DM has been found to exhibit the most promising performance in terms of selectivity and OFF current. In addition to the crossbar array integration, DM devices, due to their distinctive device dynamics, are implemented in emerging systems, *e.g.* true random number generators,²⁷ steep subthreshold slope transistors,^{30, 33} and artificial synaptic devices.^{28-29, 37}

The reported DM devices can be classified into Ag^{7, 25-40} and Cu⁴⁰⁻⁴⁵ based devices. DM devices work based on the electric field induced migration of active metal atoms, *e.g.* Cu and Ag, with high mobility inside dielectric layer. The device is switched ON when the applied electric field exceeds the threshold field required to form unstable metallic filament within the dielectric and is switched OFF due to its dissolution after the removal of electric field. This mechanism is analogous to electrochemical metallization (ECM) cells. The same structure might exhibit both non-volatile and volatile switching characteristics, which can be used for memory and threshold switch applications respectively.^{35, 44} Thus, complete control over these two opposite characteristics must be thoroughly investigated.

In this work, gradual electroforming process from pristine Pt/HfO_x/Cu/Pt structure is introduced to achieve volatile threshold switching rather than non-volatile memory characteristics. Crosspoint device structures of 10 μm × 10 μm cell area, shown in **Figure 1**, were fabricated by a two-step UV-lithography patterning followed by lift-off processes. All layers of the materials were deposited via magnetron sputtering deposition, *i.e.* DC sputtering for metals and RF sputtering from ceramic target (HfO₂) for the oxide layer. The thickness of each layer in the structure is 10nm. The electrical characterizations were done using Keithley 4200A-SCS Parameter Analyzer, *i.e.* Source Measure Unit (SMU) and preamplifier for DC IV measurement and Pulse Measure Unit (PMU) for fast IV measurement.

Gradual forming process and threshold switching characteristics of DM

In order to specifically achieve threshold switching properties, two common fabrication techniques have been implemented. The first technique involves co-sputtering and/or reactive sputtering deposition to form metal (Cu or Ag) and insulating host composites. It requires high control over the number of metal atoms within the insulating host. The second technique utilises a

post-annealing treatment to allow metal atoms diffusion into insulating layer. Temperature and duration of the annealing process are the two critical parameters to achieve the desired properties. Due to the bulk nature of the atomic diffusion, it usually requires an insertion of a thin tunnelling layer to maintain the high selectivity of the threshold switch. HfO_x/Cu-based structures have been reported as to exhibit both memristive and threshold switching properties within one structure. This technique was implemented to alter the memristive property of the device into volatile threshold switching characteristics.⁴⁴ However, the temporal response of the device has not been discussed.

It has been reported that the compliance current (CC) during the operation of DM plays an important role in controlling the nature of metallic filament induced under external electric field.^{26, 35, 45} Relatively higher CCs have been observed to result in non-volatile memory switching behaviour, while the lower CCs lead to unstable metallic filament resulting in volatile threshold switching characteristics. For the structure investigated in this work, the ON state current target was set to be 10 μ A or higher, which was based on the common switching current range reported for memristive devices. The devices underwent direct forming using compliance current of 10 μ A or higher tend to form strong conductive filament, which resulted in non-volatile switching behaviour, depicted in **Figure 2**

The electroforming process was performed by gradually increasing the CC from 100 nA to 10 μ A with certain subsequent CC ratio. Two critical parameters in the gradual forming treatment are the starting CC value and the subsequent CC ratio. It was found that the optimized forming condition to achieve stable volatile threshold switching characteristics were with the starting CC of 100 nA and subsequent CC ratio from 2 to 40. More detailed discussion on the implementation of the gradual forming treatment can be found in the supporting information section.

During the gradual forming treatment, the devices had to undergo long duration of voltage stress under DC sweep. Any structural changes exhibited by the device during this forming process is critical for the subsequent device operation. Thus, single run and multiple runs (50 cycles) of DC gradual forming treatment for each CC value were conducted to investigate the device structural changes during the forming process.

The gradual forming process allows more controllable and localized metallic filament of ionizable Cu electrode into HfO_x dielectric, shown in **Figure 3**. A decreasing trend in the threshold voltage (V_{th}) of the device was observed with increasing CC value under DC IV sweep, as shown in **Figure 4a** and **4b**. This is potentially attributed to the amount of Cu atoms residing within dielectric and the effective thickness of the oxide involve during the switching process, which is discussed further in the following segment of the work. After the gradual forming treatment was performed, the device under test was connected to series resistor of 47 k Ω to facilitate subsequent DC cycling and pulse measurements. The forming process was able to successfully achieve stable threshold switching behaviour with more than 100 DC cycles (few selected cycles are shown in **Figure 5**).

The devices tested also preserved unidirectional characteristics after forming and the subsequent cycles. The unidirectionality of the switching is due to the asymmetrical structure of the devices and the nature of the Cu filament growth within the HfO_x . There are two possible growth mechanisms in Cu-based devices, i.e. filamentary growth of Cu atoms from the active copper electrode towards the inert electrode,⁴⁶ and filamentary growth in opposite direction.⁴⁷ This suggests the localized filamentary growth of Cu atoms from the active copper electrode towards the inert electrode,⁴⁶ rather than the localized filamentary growth in opposite direction during gradual forming of the device.⁴⁷ Asymmetrical structures exhibiting bidirectional volatile

switching behaviour have only been reported in Ag-based devices.^{25, 48-49} This is consistent with reported literatures on the observation of Ag filament growth.^{35, 50} The Ag conductive filaments tend to grow from the inert electrode towards the active electrode. Thus, when the unstable filament formed during volatile switching process, the rupture of the filament does not occur at the furthest Ag atoms position from active electrode, which will leave Ag atoms residue on the inert electrode. After the first few switching cycles of the Ag-based DM devices, there will be sufficient amount of Ag atoms on both side of the dielectric to achieve bidirectional volatile threshold switching behaviour. This asymmetrical structure will not be able to achieve bidirectional selector behaviour in as fabricated devices.

Temporal response of DM devices

The underlying mechanism of DM utilises the ionic movement of the active electrode inside dielectric. While it results in an ultra-low OFF current and high selectivity, it also leads to the device having a finite delay and relaxation time during ON and OFF operations respectively. The reported values for delay time vary from about 70 ns up to 70 ms, while the relaxation time varies from 70 ns to 25 s.⁴⁸ This temporal response of the device is determined by the specific structure used, applied electric field, and device operating temperature. The focus of this study is on the influence of applied electric field amplitude on the temporal response of the devices.

The time domain measurements were performed by sending higher amplitude voltage pulse to turn ON the DM followed by a “read” pulse of 0.1 V with 20 ms pulse width after 1 μ s interval, while the current flowing through the device was simultaneously measured. **Figure 6b** shows a complete ON-OFF cycle of the device. The delay time of the device was captured through the time domain measurement from the moment “write” pulse implemented until the observation of abrupt increase in cell current, as depicted in **Figure 6a**. On the other hand, the finite relaxation time was

measured from the timestamp of the removal of the electric field until the sudden drop in cell current was observed, as shown in **Figure 6c**.

Different pulse amplitudes were implemented from 0.3 V to 1.0 V with 10 ms duration to measure the device delay time dependence on external electric field. The delay time decreases exponentially with an increase in external bias amplitude for the different devices under two different forming treatments. This correlation is supported by the field-induced nucleation theory, depicted in **Figure 7**.^{7, 51-53} Based on this theory, the metallic filament within the dielectric under an external electric field is caused by the growth of spheroidal metallic nucleus from ionic movements of active electrode atoms inside the dielectric. Stable spheroidal metallic nucleus can only be established if the nucleation energy barrier, $U_N(E)$, is overcome to allow the nucleus growth beyond critical radius R_N . This energy barrier is reduced with the presence of external electric field and will return to its equilibrium value, U_0 , after the removal of the field. It has been reported that the nucleation leads to volatile switching characteristics if the effective radius of the stable nucleus is lower than R_0 , while resulting in non-volatile switching behaviour if it increases past R_0 . The delay time of the device can be correlated to the nucleation energy barrier height with the following equation,⁷

$$\tau_d = \tau_0 \exp \left[\frac{U_N(E)}{kT} \right] . \quad (1)$$

The temperature of the devices was kept constant at room temperature throughout the experiment. τ_0 is defined as the characteristic delay time, which is unique to the active material and dielectric used in the system. $U_N(E)$ is defined as nucleation energy barrier height, that can be expressed as the following,

$$U_N(E) = U_0 E_0 \alpha^{\frac{3}{2}} \frac{d}{V} . \quad (2)$$

V and d are defined as external voltage applied and effective thickness of the dielectric involved during the volatile switching operation. The effective thickness refers to smallest distance between the Cu atoms to the Pt inert electrode across the dielectric. U_0 is defined as the nucleation barrier energy at zero-field, which is unique to the dielectric material in which the metal atoms move within, e.g. HfO_x (0.47 eV) and TiO_x (0.71 eV).⁷ In this work, the dielectric material used was the same, i.e. HfO_x . Thus, under the two forming treatments, the value of parameter U_0 did not change. E_0 is defined in literatures as voltage acceleration factor or characteristic field. This value is independent of the external field or temperature. The acceptable value used in calculation is 1 MV/cm,⁷ regardless of the type of structures or systems. α is geometric factor of spheroid nucleus. Its value ranges from 0.1 to 0.5 and it was assumed to be 0.5 in the literature because it corresponds to the highest nucleation barrier energy. This value is dependent on the shape of the nucleus. Across different dielectric materials, this value might be different, but within the same dielectric material, this geometric factor can be safely assumed to be identical.

The focus of this segment of the work is to investigate the effect of external electric field (voltage) on the temporal response of the device. Hence, to simplify the expression in (1), another critical parameter ζ is defined to replace $U_N(E)$.

$$\zeta = U_0 E_0 \alpha^{\frac{3}{2}} \frac{d}{kT} . \quad (3)$$

Thus, equation (1) can be modified into the following,

$$\tau_d = \tau_0 \exp \left[\frac{\zeta}{V} \right] . \quad (4)$$

Equation (4) was used to fit the experimental data obtained for device delay time under different pulse amplitude, shown in **Figure 8**. The experimental data fits well under field-induced nucleation theory with a spheroidal-shape metallic filament. The device delay time varies from approximately 5 ms to under 300 μ s for the single run forming treatment, while it ranges from 250 μ s to as fast as 44 μ s for multiple runs forming treatment under different voltage amplitudes. Two parameters could be extracted from the fitting curves, i.e. τ_0 and ζ . τ_0 values extracted from the fitting are ~ 19 μ s and ~ 21 μ s for devices underwent single and multiple forming treatments respectively. This is consistent with the two forming conditions being strictly comparing the same Pt/HfO_x/Cu/Pt structures. On the other hand, the extracted ζ values under two different forming treatments exhibit a significant difference. Based on the field nucleation theory, it is attributed to the change in the effective thickness of the oxide layer involved throughout the nucleation process. It was found that the value of ζ_1 is about 4 times higher than ζ_2 . The devices underwent single forming treatment was assumed to have very small change in the effective thickness from the pristine devices, i.e. ~ 10 nm. The thickness of the HfO_x layer in the pristine devices was experimentally confirmed by TEM images of the multilayer structure, as shown in **Figure S3**. This indicates the effective thickness of the oxide was reduced significantly from ~ 10 nm originally to ~ 2.5 nm.

The relaxation time of the device was also investigated under different voltage amplitude in the range of 0.8 V-1.2 V with 10 ms pulse width. From **Figure 9**, an increasing trend of relaxation time was observed from about 1 ms to 7 ms with an increase of voltage amplitudes. This trend is potentially due to the size of the spheroidal nucleus generated under different voltage pulses. The higher the amplitude of the pulse, the stronger or larger metallic nucleus dimension formed. Thus, larger metallic nucleus will take a relatively longer time to rupture after the removal of electric field.

This observation is supported by the Rayleigh instability model of the metallic filament rupture inside dielectric.^{26, 36-37, 40} Rayleigh instability suggests that after a removal of an electric field, the metallic filament ruptures into series of spherical nanoclusters through the minimization of total free energy of the system. With our earlier confirmation on spheroidal metallic nucleus growth by looking at the device delay time dependency on voltage pulse amplitude, the initial filament shape before the removal of electric field is taken as spheroid, as shown in **Figure 10**. Thus, an analytical model was proposed better understand the evolution of filament morphology. After the removal of electric field, the spheroidal nucleus is divided into N number of nanospheres. This process is assumed to be due to the atomistic re-arrangement of Cu atoms, causing the total volume of the shape to be constant throughout the process. The number of Cu spherical nanoclusters (N) formed can be expressed as,

$$N = \rho \frac{R^3}{D^3}, \quad (5)$$

where ρ is defined as aspect ratio of L/R , in which L and R the initial major and minor axis dimension of the nucleus respectively. D is defined as the average diameter of nanoclusters formed in the OFF state of the device. This phase transition is driven by the change in total free energy consists of both surface and volume terms. However, with the assumption of constant volume throughout the process, the change in surface free energy will be the only terms contributing into the system. By approximation of very thin metallic filament ($\rho \gg 1$), the change in free energy was estimated in the following:

$$\Delta G \approx \pi \rho R^2 \left(\frac{R}{D} - \frac{\pi}{4} \right). \quad (6)$$

Spontaneous evolution of the filament after the removal of the electric field has been experimentally confirmed in the rupture of Ag filament as per this literature.²⁶ Thus, the change in

free energy should be less than zero and the dimension of the nanoclusters should follow this relation:

$$D > \frac{4}{\pi} R. \quad (7)$$

After applying longitudinal damped sinusoidal perturbation along the major axis of the spheroid, the surface perturbation equation is given by:

$$r(z, t) = R(z) + \delta_2(t)\delta_1(z) \sin kz, \quad (8)$$

where k is the perturbation wavenumber along the z -axis, $\delta_1(z)$ and $\delta_2(t)$ are the spatial and temporal dependence of the perturbation amplitude terms respectively. While the temporal dependence of the perturbation amplitude has been frequently reported,^{26, 36-37, 40} the spatial dependence of the amplitude was added due to the spheroidal nature of the filament. If $z = z_N$ was taken as the centre point of one of the nanospheres, the relaxation time of the device is determined by the following equation:

$$\delta_2(\tau_d) = \frac{D - R(z_N)}{\delta_1(z_N) \sin kz_N}. \quad (9)$$

From this equation, it was concluded that the relaxation time is mainly driven by initial filament profile, which is driven by the current or voltage amplitude during the “write” operation.

Reliability aspects of DM: device endurance and observation of random telegraph signal (RTS)

The endurance test was performed on the device which underwent multiple runs of forming treatment. By using the correlation of pulse amplitude to the delay time of the device in **Figure 8**, the endurance test was performed by sending 200 μ s of 0.4 V pulse to turn ON the device and 200 μ s of 0.2 V pulse to measure the OFF state of the device. The OFF state of the device was beyond

the measurement limit of the equipment. No selectivity degradation was observed after more than 10^4 cycles, shown in **Figure 11**. The current distribution of the ON state was observed to be lower than the current flow of 1-Resistor under the same voltage, which means the DM device reached a comparable resistance value to that of the resistor as expected. However, the distribution of the current of DM device was noticeably asymmetrical and has broader variation compared to 1-Resistor current.

The origin of the ON-state current variation is explained by the presence of random telegraph signal (RTS) in DM devices. RTS is defined as a random bimodal or multilevel fluctuation of current or voltage during device operation. RTS has been widely reported in memristive devices, especially oxide-based devices utilising the movement of oxygen ions and/or oxygen vacancy-type defects modification for its operations. For these types of devices, the origin of the RTS is believed to be from the reversible movement of electrons between metal electrodes and defects within dielectric layer which is also known as charge trapping and de-trapping activities.⁵⁴ However, DM device structure and underlying switching mechanism mimics those of electrochemical metallization cells (ECM). Thus, the origin of RTS in DM devices is expected to incline towards those similar type of devices in which very few studies have been conducted. In Cu doped $\text{Ge}_{0.3}\text{Se}_{0.7}$ devices, it is suggested that the RTS presence in the device is potentially due to thermally activated movement of Cu species within ionic or redox “double-site traps”.⁵⁵ Another report on $\text{Ge}_x\text{Se}_{1-x}$ -based devices showing the observation of RTS in ionic threshold switching mechanism after the forming process.⁵⁶ **Figure 12** shows different RTS observed in the DM structure during the ON state of the device under 0.4 V voltage amplitude. Both bimodal and multilevel RTS was observed within the same structure but under different writing cycles. This demonstrated the random and complex nature of the signal. The current readings of the device ON and OFF states

during the endurance test were done by taking the average of the data points at the same 10 μ s window. Thus, with the time domain variation of RTS, the cell current distribution would be larger than the current distribution of 1-R configuration.

Further investigation of the RTS behaviour was performed under different applied voltage amplitudes. Two different types of RTS were observed in different voltage regimes, depicted in **Figure 13**. The first RTS was more dominantly observed in the low voltage regime (≤ 0.6 V), resulting in random fluctuations throughout the ON state of the device. It was the same type of RTS causing the current distribution broadening during endurance test at 0.4 V. This RTS became less apparent with the increase of the external applied voltage. The second RTS was observed in the high voltage regime of more than 0.6 V. This RTS was more likely to be observed in the early stage of the ON state rather than throughout the ON state. This could be attributed to the competing nature of the two parameters, *i.e.* external electric field and Joule heating. Higher electric field tends to result in stronger filament but at the same time it will generate larger Joule heating effect that might rupture the metal filament. The current reading was observed to stabilize after several current jumps. This could be an indication of a stronger and larger filament had been formed after several ruptures. This property must be taken into consideration in the device implementation as a select device in crossbar array, especially during the “write” operation of the memory cell that requires higher voltage amplitude. The average time constant of this behaviour was above 10 μ s. Thus, it will not affect the memory operation of the devices operating in the faster regime in which most of the reported memristive devices stand.

Conclusions

This work has provided a new technique, from device operation point of view, to achieve volatile threshold switching behaviour from pristine Pt/HfO_x/Cu/Pt structure via gradual electroforming treatment. Excellent selectivity of more than 10^7 and extremely low OFF current of 100 fA were maintained with more than 10^4 ON-OFF cycles. An insight into the structural evolution of the DM was discussed by analysing the temporal response of the device under different external electric fields in the frame of the field-induced nucleation theory and Rayleigh instability model. This analysis can be potentially used to extrapolate the device degradation mechanism in which excessive amount of copper species eventually reside within the insulating layer. The reliability aspect of the device considering the current distribution broadening observed during endurance test was also discussed. It was caused by the presence of RTS originated from thermally induced Cu ionic or redox “double-site traps” activities in the structure. The RTS dependence on external applied voltages was also investigated, which gives an important insight on the time domain behaviour of the device under different voltage regime.

ASSOCIATED CONTENT

Supporting Information

The volatile threshold switching characteristics achieved under 100 nA and 1 μ A without gradual forming treatment (**Figure S1**); The characteristics of the devices under gradual forming treatment with starting CC of 100 nA and subsequent CC ratio of 2 and 40 (**Figure S2**); The behaviour of the devices under starting CC of 100 nA and subsequent CC ratio of 40 (**Figure S3**); Cross-sectional TEM image of the pristine $10 \times 10 \mu\text{m}^2$ device (**Figure S4**)

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Author Contributions

Putu A. Dananjaya and Samuel C.W fabricated the devices. Putu A. Dananjaya conducted the measurements. Putu A. Dananjaya, Desmond J. J. Loy, Samuel C. W. Chow, and Wen S. Lew wrote the manuscript. All authors have approved the final version of the manuscript

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Figures and Captions

Figure 1. (a) Top view of the crosspoint device under optical microscope. (b) 3D view of the structure taken by atomic force microscopy

Figure 2. The behaviour of the devices underwent direct electroforming under $10 \mu\text{A}$ CC showed a mix of volatile and non-volatile switching behaviour in between cycles (**Figure 2a**), while the devices underwent gradual forming treatment exhibited pure volatile threshold switching characteristics (**Figure 2b**).

Figure 3. Gradual forming process of the device from the lowest compliance current (a) to the highest one (c)

Figure 4. (a) DC IV sweep of gradual forming treatment. (b) Decreasing trend of threshold voltage with the increase of compliance current

Figure 5. DC IV sweep with series resistor of 47 k Ω connected to the DM device shows the unidirectionality of the DM devices. Ultra-low OFF state current about 100fA and high selectivity of 10^7 was observed under V/2 operating scheme.

Figure 6. Complete ON-OFF cycle of the time domain measurement of the device (**Figure 6b**) to capture device delay time (**Figure 6a**) and device relaxation time (**Figure 6c**).

Figure 9. Increasing trend of average relaxation time of the device observed under increasing voltage pulse amplitude

Figure 10. Metallic filament dissolution process based on Rayleigh instability theorem

Figure 11. (a) Actual endurance cycle reading of the device with over 10^4 ON-OFF cycles. (b) Comparison of current distribution between 1-DM-1Resistor and 1-Resistor under 0.4V voltage amplitude.

Figure 12. RTS captured from different cycles operation of the device during the ON state under 0.4V voltage amplitude. Unstable complex RTS were observed exhibiting multilevel RTS nature.

Figure 13. The RTS behaviour was observed under different voltage amplitudes. Red-dashed lines are the current peak due to measurement settling time and black-dashed line indicates the current flow of the 1-R configuration (taking current reading of 1.0V as an example).