Oxygen Vacancy Density Dependence with a Hopping Conduction Mechanism in Multilevel Switching Behavior of HfO$_2$-Based Resistive Random Access Memory Devices

Desmond J. J. Loy, Putu A. Dananjaya, Somsubahra Chakrabarti, Kuan Hong Tan, Samuel C. W. Chow, Eng Huat Toh, and Wen Siang Lew*

ABSTRACT: We report a switching model that directly explains the change in activation energy ($E_{\text{AC}}$) at different RESET stop voltages ($V_{\text{stop}}$) in HfO$_2$-based resistive random access memory devices. The dependence of oxygen vacancy-driven conductive filaments ($V_{\text{fil}}^{\text{o}_2}$) density ($n_{\text{fil}}$) on $V_{\text{stop}}$ was validated by a kinetic Monte Carlo (kMC) simulation and hopping conduction mechanism. A wide operating range of temperatures from $-40$ to $175$ °C is achieved with stable endurance of 100 ns short pulses and high retention of more than 10 years at $125$ °C. Distinct exponentially increased multilevel high-resistance states are observed at increasing $V_{\text{stop}}$ and is attributed to the increase in $E_{\text{AC}}$ with $V_{\text{stop}}$. The increase in $E_{\text{AC}}$ due to the increase in $V_{\text{stop}}$ and depletion of $n_{\text{fil}}$ during RESET was explained using our proposed switching model. A kMC simulation further emphasizes this relation due to the depletion of $V_{\text{fil}}^{\text{o}_2}$ during RESET, which was supported by the increase in trap-to-trap distance in the hopping conduction analysis.

KEYWORDS: RRAM, oxygen vacancy density, kinetic Monte Carlo, hopping conduction, high retention, multilevel switching, activation energy, wide operating temperature range

INTRODUCTION

Resistive random access memory (RRAM) has been one of the most optimistic non-volatile memories, largely attributed to its simple metal–insulator–metal (MIM) structure, high speed and low power, high scalability, high density, and high endurance and retention capabilities, along with its high complementary metal oxide semiconductor (CMOS) compatibility. Oxide-based RRAM devices are the most widely studied due to their dielectric properties in MIM structures in creating memory states from the commonly investigated metallic or oxygen vacancy-driven conductive filaments ($V_{\text{fil}}^{\text{o}_2}$). The details of these switching mechanisms are being debated, but there is strong evidence where device, stack, and/or thickness engineering could alter the switching mechanism of the RRAM. Among all the oxides, high-$k$ HfO$_x$ is widely studied as it is CMOS friendly and has been established as gate dielectrics in state-of-the-art logic and memory devices. HfO$_x$ is also a great candidate due its good thermal stability and recently in its multilevel state properties when used as a dielectric of a switching element. In traditional memory, there exists two states of “1” and “0”, which represents the low resistance state (LRS) and high resistance state (HRS), respectively. However, to keep up with the ever-growing digital age where data consumption and generation are growing at an exponential rate, there is an increasingly strong need to advance toward multi-bit to enhance the storage scalability of modern-day memory devices and to delve deeper into neuromorphic applications. Over the past few decades, there have been numerous works focusing on the modeling studies of multitemperature and multilevel states in resistive switching devices. A physical model and a thermally activated hopping model were proposed by Ielmini for multilevel state filament growth and ion migration. Similarly, a physical model was applied by Bousoulas et al. to highlight the local electric field and temperature profiles of SET/RESET transitions. Numerical models were also proposed by Larentis et al. and Kim et al. to explore temperature and field-accelerated migration of $V_{\text{fil}}^{\text{o}_2}$. Arrhenius equation models were also investigated by Chiu et al. to highlight the local electric field and temperature profiles of SET/RESET transitions. Furthermore, a negative voltage-modulated multilevel resistive switching during reset was observed and explained using conduction mechanisms by Chakrabarti et al. and Samanta et al. On a similar note, temperature-dependent conduction

Received: June 16, 2020  
Accepted: September 18, 2020  
Published: September 18, 2020
mechanisms were used by Bai et al. to explain the \( V_{\text{O}2^+} \) evolution at different multilevel states.\(^{32}\) A \( V_{\text{O}2^+} \) evolution model was also proposed by Qi et al. to explain the dendritic filament under different negative electric fields.\(^{33}\) Although these works of literature exhibit various methods of explaining filament evolution in multilevel states, there have been limited physics understanding on the behavior and density of oxygen vacancies (\( n_D \)) at different stopping reset voltages (\( V_{\text{stop}} \)). Such a study is important because a combination of experimental and theoretical aspects will provide a more comprehensive understanding of filament evolution in multilevel state RRAM.

We validate the multilevel state switching of Pt/HfO\(_2\)/Ti resistive switching devices with our proposed activation energy (\( E_{\text{AC}} \)) and \( V_{\text{stop}} \) switching model in this work. In particular, the \( E_{\text{AC}} \) of HfO\(_2\) can be obtained from an Arrhenius equation fitting and was used to explain the relationship between \( V_{\text{stop}} \) and \( n_D \). We explored the switching, endurance, and retention characteristics of Pt/HfO\(_2\)/Ti resistive switching devices to better understand their performance. In addition, TEM and XPS analysis were performed to investigate the uniformity of deposited films and their crystallinity. Temperature studies ranging from \(-40\) to \(175^\circ\)C were also performed to investigate the \( I-V \) characteristics for applications such as automotive and sensors in different weather conditions. Multilevel states were also investigated by varying \( V_{\text{stop}} \) from \(-0.9\) to \(-1.3\) V at intervals of \(-0.1\) V. A kinetic Monte Carlo (kMC) simulation of Pt/HfO\(_2\)/Ti RRAMs at various \( V_{\text{stop}} \) also exhibited an inverse relation with the number of oxygen vacancies (\( n_o \)) at different parts of the filament. This model was further validated by the hopping conduction analysis in the bulk region of the Pt/HfO\(_2\)/Ti resistive switching devices, where the increments in the trap-to-trap distance (\( a \)) were observed with increasing \( V_{\text{stop}} \).

**EXPERIMENTAL METHODS**

Pt(10 nm)/HfO\(_2\)(10 nm)/Ti(100 nm) resistive switching structures were grown on Si/SiO\(_2\) substrates using magnetron sputtering deposition techniques. The chamber base pressure was lower than \(2 \times 10^{-8}\) Torr, and the sputter pressure was 2 mTorr with 20 sccm of Ar flow rate. The stacks were patterned into \(10 \mu\m \times 10 \mu\m\) devices in a combination of UV lithography and ion-milling processes. A two-step lithography process was used to form a cross pattern of the device junction. These fabrication processes were described in detail from steps 1 to 13 as shown in Figure 1. Current–voltage (\( I-V \)) measurements were performed using a Keithley 4200 semiconductor parameter analyzer.

**CURRENT–VOLTAGE, ENDURANCE, AND RETENTION INVESTIGATIONS OF Pt/HfO\(_2\)/Ti RRAM DEVICES**

The \( I-V \) behavior of Pt/HfO\(_2\)/Ti resistive switching devices was investigated to better understand the switching characteristics and HRS multilevel switching properties. Consistent switching could be observed in Figure 2a where \(50 I-V\) cycles of one device was plotted. In the \(50 I-V\) cycles, it was found that

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**Figure 1.** Fabrication process of Pt/HfO\(_2\)/Ti RRAM devices consisting of a two-step lithography, etching, and deposition processes.

**Figure 2.** (a) Semi-log \( I-V \) plots of Pt/HfO\(_2\)/Ti resistive switching devices showing the forming process and the first 50 \( I-V \) switching cycles at an ON/OFF ratio of \(-50 \times\). (b) Resistance box plot of Pt/HfO\(_2\)/Ti resistive switching devices exhibiting some device-to-device variability.
the average SET voltage is 0.5 V at a compliance current of 700 μA, while the \( V_{\text{stop}} \) is fixed at \(-1.2 \) V, giving an ON/OFF ratio of about 50×. The forming voltage was observed to be at 1.8 V at a compliance current of 1 mA. While there was consistent switching and low cycle-to-cycle variability, it was more important to observe the presence of gradual switching characteristics in the RESET state, thus confirming the existence of multilevel states in the HRS.\(^{34,35}\) In the investigation of multiple device characteristics, the device-to-device variability of the resistive switching devices with an average SET voltage of 0.5 V and \( V_{\text{stop}} \) at \(-1.2 \) V was also shown in a resistance box plot in Figure 2b, read at \(-0.1 \) V. It was found that the median ON/OFF ratio was about 50×, a ratio large enough for multiple level resistance switching states to occur.

Endurance studies were also performed at SET/RESET pulse heights of 0.6 V/\(-1.3 \) V at 100 ns pulse widths as shown in the flow chart of Figure 3a. Two read/write schemes A and B were implemented at different cycles as shown in the flow charts of Figure 3a,b. While scheme A was implemented to every (1st, 2nd, 5th) \( \times \) 10\(^n\) cycle where \( n = 0, 1, 2, 3, \) and 4, scheme B was implemented to every cycle in between. Scheme A reads the resistance state after every SET and RESET write, while scheme B adopts a current-blind pulsed voltage stress (PVS) method where there is only SET and RESET writing but no reading.\(^{36}\) At least 5 \( \times \) 10\(^5\) endurance cycles at an average ON/OFF ratio of 50× were observed as the LRS converged to the HRS at the 10\(^6\)th cycle. (d) Arrhenius plot showing that the retention exceeds 10 years at 125 °C.

**Figure 3.** (a) Read/write schemes of endurance performed at SET/RESET pulse heights of 0.6 V/\(-1.3 \) V at 100 ns pulse widths. (b) Endurance flow chart where scheme A was implemented to every (1st, 2nd, 5th) \( \times \) 10\(^n\) cycle where \( n = 0, 1, 2, 3, \) and 4, while scheme B was implemented to every cycle in between. (c) At least 5 \( \times \) 10\(^5\) endurance cycles with an \(~50\times\) ON/OFF ratio where LRS converged to the HRS at the 10\(^6\)th cycle. (d) Arrhenius plot showing that the retention exceeds 10 years at 125 °C.

**Figure 4.** (a) TEM image of Pt/HfO\(_2\)/Ti resistive switching devices showing uniformly deposited layers. (b) Characteristic XPS profile of O 1s showing two oxygen states indicating 4.79% of oxygen vacancies with the XPS profile of Hf 4f (inset) of HfO\(_2\) films.
first switched to LRS and heated up to 310, 330, and 350 °C while checking their resistance state using a read voltage of −0.1 V. The device is considered failed when the device switched to the HRS unintentionally, and its corresponding time to fail was recorded. These three temperature points were plotted and extrapolated to 10 years (≈3.154 × 10^8 s). From the extrapolation, it was observed that the retention exceeds 10 years at 125 °C, exhibiting strong retention capabilities in Pt/HfO₂/Ti RRAM devices. The activation energy (E_a) was also extracted to be 1.72 eV, which is higher than 0.6 eV of FLASH. However, the pre-exponential factor B varies with different types of insulators and electrode materials, thus producing different E_a.

**XPS AND TEM CHARACTERIZATIONS OF PT/HF02/TI RRAM DEVICES**

Material studies such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were also...
performed on Pt/HfO₂/Ti resistive switching devices and HfOₓ films, respectively. TEM was performed on the devices to investigate the uniformity of deposited films and their crystallinity, while XPS studies were performed on HfO₂ films to verify the Hf and O peaks. The TEM analysis in Figure 4a exhibited uniformly deposited RRAM layers with the inset of Figure 4a showing an amorphous HfOₓ structure.

Figure 7. Semi-log I–V plots of Pt/HfO₂/Ti resistive switching devices with $V_{\text{stop}}$ at (a) −0.9, (b) −1.0, (c) −1.1, (d) −1.2, and (e) −1.3 V, indicating an increasing HRS trend. (f) Mean of each semi-log I–V plot from panels (a–e) and (g) their corresponding cumulative probability plot at $V_{\text{read}} = −0.1$ V of 200 I–V cycles in each voltage of −0.9 to −1.3 V at intervals of −0.1 V. (h) $R_{\text{HRS}}$ vs. $V_{\text{stop}}$ with an exponential fit with 25th–75th percentile as the range of error bars.
In the XPS profiles, broad and overlapping O 1s peaks and well-separated spin–orbit Hf 4f peaks were shown in Figure 4b and its inset, respectively. The deconvolution of the Gaussian O 1s spectrum revealed two different oxygen components of binding energies 530.0 and 531.8 eV, respectively, as shown in Figure 4b. While the 530.0 eV peak characteristic to $O^{2-}$, the higher binding energy of 531.8 eV can be attributed to $O^{2+}$.

The amount of oxygen vacancies was found to be 4.79% of the entire oxygen content of the HfO$_2$ material by taking the proportion of areas under the two oxygen peaks in Figure 4b. Similarly, the binding energies of the Hf 4f peaks were found to be 16.8 and 18.3 eV as shown in the inset of Figure 4b, which were characteristic to Hf. While Burrell et al. discussed about using spectral peak energy, intensity, and structural analysis to determine the composition and chemical state of the material species, Luo et al. performed XPS on their HfO$_2$ films by capturing the energy of X-ray-ejected photoelectrons emitting specific to the chemical state and compounds. These analyses culminated in the area calculations under the material profiles such that by comparing the areas under the curve of the O 1s and Hf 4f profiles, the atomic concentrations revealed a stoichiometry of HfO$_2$ with an error of 0.25%.

### TEMPERATURE CHARACTERIZATION AND ARRHENIUS EQUATION RELATION BETWEEN THE HIGH RESISTANCE STATE AND TEMPERATURE

Various temperature studies were performed at −40, 25, 75, and 125 °C, and 50 cycles of I–V curves were measured at each temperature as shown in Figure 5a–d, respectively, with average curves in red.$^{51}$ The SET voltage ranged from 0.5 to 0.75 V, the RESET voltage was −1.2 V, while the ON/OFF ratio is about 50× at the same $V_{\text{read}}$ at −0.1 V. The RESET processes have shown stable HRS switching and maintained ~50× ON/OFF ratio at −40, 25, 75, and 125 °C. These observations indicated a good thermal stability in Pt/HfO$_2$/Ti resistive switching devices in the HRS even at low temperatures, indicating that the multilevel HRS is resilient at different temperature ranges.

Further temperature studies at −40, 25, 75, 125, and 175 °C were also performed on devices 1, 2, and 3 to investigate the full operating range of Pt/HfO$_2$/Ti RRAM devices. An $I–V$ sweep of −0.6 to 0.6 V was performed on devices 1, 2, and 3 where the HRS decreases with an increasing temperature trend as shown in Figure 6a–c, respectively. For each of these devices, the HRS values were extracted at each temperature point at a randomly selected low $V_{\text{read}}$ of 0.4 V. Thereafter, an Arrhenius equation indicated by eq 1 was linearly fitted on those extracted points as shown in Figure 6d by taking a natural logarithm on both sides of eq 1:

\[
R_{\text{HRS}} \equiv R_0 \exp\left(\frac{E_{\text{AC}}}{kT}\right).
\]

where $R_{\text{HRS}}$ is the HRS, $R_0$ is the pre-exponential factor, $E_{\text{AC}}$ is the activation energy of HfO$_2$, $k$ is the Boltzmann constant, and $T$ is the corresponding temperature of the performed measurement. The value of $R_0$ is inversely related to $n_{\text{D}}$ which is indicative of the $n_{\text{D}}$ present in Pt/HfO$_2$/Ti devices and is characteristic to different RRAM stack configurations. Eq 1 shows that $R_0$ is proportional to $R_{\text{HRS}}$ thus making $R_{\text{HRS}}$ inversely related to $n_{\text{D}}$. At the same time, eq 1 also shows that $R_{\text{HRS}}$ is inversely proportional to temperature,$^{38}$ which would result in the increase in $n_{\text{D}}$ with increasing temperature. More intuitively, $n_{\text{D}}$ increases with increasing temperature because a higher temperature lowers the resistance of the RRAM device, which increases $n_{\text{D}}$. The decreased resistance of the device could be attributed to a less significant filament rupture, which in turn is caused by a higher $n_{\text{D}}$. A less significant rupture is represented by a lower extent of recombination between $O^{2-}$ and $V_{o}^{2+}$, thus causing the density of $V_{o}^{2+}$ to be higher, i.e., $n_{\text{D}}$ is higher. $E_{\text{AC}}$ and $R_0$ were found to exhibit average values of 0.022 eV and 152.18 Ω, respectively from the fittings shown in Figure 6d. The value of $E_{\text{AC}}$ was also found to be at a consistent range to the values reported by Larcher et al. and Bersuker et al. for HfO$_{x}$ based devices.$^{46,47}$ The $R_{\text{HRS}}$ versus 1/T trend has remained similar for all three devices, indicating that $R_{\text{HRS}}$ increases with decreasing temperature.

### SWITCHING MODEL BETWEEN ACTIVATION ENERGY, RESET STOPPING VOLTAGE, AND RESET MULTILEVEL RESISTANCE STATES

The $E_{\text{AC}}$ of HfO$_2$ was further investigated with $n_{\text{D}}$, which changes with $V_{\text{stop}}$. Multilevel states were explored by varying the $V_{\text{stop}}$ from −0.9 to −1.3 V at intervals of −0.1 V as shown in Figure 7a–e, respectively. It could be observed that as the $V_{\text{stop}}$ increases from −0.9 to −1.3 V, the HRS increases, and $n_{\text{D}}$ decreases. Further investigations of the multilevel states were performed where 200 $I–V$ cycles in each voltage of −0.9 to −1.3 V at intervals of −0.1 V shown in Figure 7a–e were averaged and combined into Figure 7f. Thereafter, the cumulative probability for all 200 $I–V$ cycles shown in Figure 7a–e were plotted at $V_{\text{read}} = −0.1$ V in Figure 7g. It can also be observed from the cumulative probability plot in Figure 7g that the HRS increased at a faster rate as voltage increases. Therefore, an exponential factor between the HRS and $V_{\text{stop}}$ could be used to explain the filament evolution and its relationship with multilevel states in eq 2:

\[
R_{\text{HRS}} = a \exp(\beta V_{\text{stop}}),
\]

where $R_{\text{HRS}}$ is again the HRS, $a$ is the constant factor of the exponential function, and $\beta$ is a factor of the exponent. $R_{\text{HRS}}$ is plotted against $V_{\text{stop}}$ in Figure 7h, $a$ was found to be 86.34, and $\beta$ was found to be 5.42 at the 50th percentile. The 25th and 75th percentiles were also plotted as the range of the error bars, mostly exhibiting non-overlap between different multilevel states. As eq 1 relates $R_{\text{HRS}}$ to $E_{\text{AC}}$ and eq 2 relates $R_{\text{HRS}}$ to $V_{\text{stop}}$, which is a function of $E_{\text{AC}}$, the relationship between $E_{\text{AC}}$ and $V_{\text{stop}}$ can be established in eq 3 by combining eqs 1 and 2:

\[
E_{\text{AC}} = [\ln(\alpha) - \ln(N_{0}^\beta)]kT + \beta V_{\text{stop}}kT
\]
KINETIC MONTE CARLO SIMULATION WITH VARYING OXYGEN VACANCY DENSITY IN DIFFERENT REGIONS OF THE FILAMENT

KMC modeling was performed on Pt/HfO$_2$/Ti devices using Ginestra, which applies comprehensive physics to simulate defect evolution, where the electric field and potential profiles were calculated by solving Poisson’s and charge continuity equations. The KMC model parameters obtained from the density functional theory (DFT) and literature were implemented. Generation, recombination, and diffusion of O$^2-$ and V$_{O}^-$ are the main processes governing the filament evolution when $V_{stop}$ was increased from 0 to $-2$ V. The assumptions of the KMC model include the following: (1) the full length of the filament runs from one end of the electrode to the other; (2) the filament gap during the rupture process is with respect to the top electrode; and (3) generation, recombination, and diffusion equations are used to describe oxygen ions and vacancies. These processes and model parameters were exhibited in the flowchart as shown in Figure 8.

In the generation of defects associated to the breakage of Hf–O bonds during the SET operation, the rate of generation of oxygen vacancies and ions $G_F$ is calculated by the thermochemical theory as shown in eq 5.

$$G_F(x, y, z) = \nu \exp \left(- \frac{E_A,D - k_B T}{k_B T} \right)$$

$$G_{R}(x, y, z) = \nu \exp \left(- \frac{E_A,R}{k_B T} \right)$$

where $\nu$ is the effective vibration frequency, $E_A$ is the zero field effective activation energy to break the metal-oxygen bond, $F$ is the electric field, $k_B$ is the Boltzmann’s constant, $p_0$ is the relative dielectric constant. Similarly, during RESET, the diffusion and recombination of carriers play an important role, and their rate can be calculated by eqs 6 and 7.

Table 1. Model Parameters Used in the KMC Model Obtained from the DFT and Literature

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<th>Parameters</th>
<th>Description</th>
<th>Value</th>
<th>Reference</th>
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<td>$r_f$</td>
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<td>$k$</td>
<td>HfO$_2$ relative dielectric constant</td>
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<td>54</td>
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<tr>
<td>$k_{\text{rel}}$</td>
<td>HfO$_2$ thermal conductivity</td>
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<td>55</td>
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<td>$v$</td>
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<td>56</td>
</tr>
<tr>
<td>$p_0$</td>
<td>O–Hf bond polarization factor</td>
<td>5.2 eV</td>
<td>56</td>
</tr>
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<td>O–Hf bond breakage zero-field effective activation energy</td>
<td>2.9 eV</td>
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</tr>
<tr>
<td>$E_{A,D}$</td>
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<td>57</td>
</tr>
<tr>
<td>$E_{A,R}$</td>
<td>recombination activation energy</td>
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<td>58</td>
</tr>
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</table>

In the validation of eq 4, a KMC simulation of Pt/HfO$_2$/Ti devices considers the molar general case of V$_{O}^-$ filament species during the RESET as shown in Figure 9a. $-1.2$ to $-2$ V were simulated, and the number of oxygen vacancies ($n_o$) versus $V_{stop}$ in Figure 9a revealed that $n_o$ remained constant at the beginning. However, when $V_{stop}$ is sufficient to overcome the oxide barrier, $n_o$ decreases linearly until it eventually saturates at a certain number. For simplicity, the filament was separated into two regions, the top 25% of the filament and the bottom 75% of the filament. Further analysis of $n_o$ at different locations of the filament at different $V_{stop}$ were also performed where the $n_o$ was obtained at the top 25% gap and bottom 75% non-gap regions of the filament as shown in Figure 9b. It was observed that $n_o$ decreases in all parts of the filament as $V_{stop}$ increases. The KMC simulation suggests that the rupture at the gap region becomes larger as $V_{stop}$ is increased from $-1.2$ to $-2$ V, as shown in Figure 9b. As $n_o$ is proportional to $n_{O}$, the KMC model validates the inverse relationship between $V_{stop}$ and $n_{O}$.

HOPPING CONDUCTION OF PT/HfO$_2$/TI RRAM DEVICES AND THE RELATION BETWEEN HOPPING DISTANCE AND RESET STOPPING VOLTAGE

While the filament rupture at the top 25% gap of the filament with increasing $V_{stop}$ is well established, the decrease in $n_{O}$ for the rest of the filament might not be as well understood. Therefore, the decrease in $n_{O}$ for the bottom 75% of the filament was further investigated using conduction mechanism studies. Although Fowler–Nordheim (FN) tunneling has been considered as one of the candidates for conduction mechanism studies, hopping...
The hopping conduction used for the analysis was shown in eq 8:

$$J = qan \exp \left( \frac{qanE - \phi_T}{kT} \right)$$  \hspace{1cm} (8)$$

where $n = 5 \times 10^{24}$ m$^{-3}$ is the electron concentration in the conduction band, $v = 2 \times 10^{13}$ Hz is the frequency of thermal vibration of electrons in the trap site, $a$ is the mean distance between traps, and $\phi_T$ is the energy level of the trap site below the conduction band. The linear fitting of hopping conduction was performed by taking the natural log on eq 8 followed by an ln($I$) versus $V$ plot as shown in Figure 10. The selected fitting voltage range of $-0.9$ to $-1.3$ V with a corresponding current range of $-2$ orders exhibited a good fit with linear correlation. Unlike the abrupt SET process found in Pt/HfO$_2$/Ti RRAM devices, the gradual RESET switching process enabled the investigation of trap-to-trap characteristics at different $V_{\text{stop}}$ and hence different multilevel states. The gradient ($M$) and vertical intercept ($C$) from eqs 9 and 10 can also be extracted from the fitting $\ln(I) = MV + C$:

$$M = \frac{qa}{kTd}$$  \hspace{1cm} (9)$$

where $d$ is the distance between the top and bottom electrode, while $a$ and $\phi_T$ can be obtained from eqs 9 and 10, respectively. The parameter $a$ extracted from eqs 9 and 10 was shown to increase as $V_{\text{stop}}$ increases from $-0.9$ to $-1.3$ V at intervals of $-0.1$ V in Table 2. As $V_{\text{stop}}$ increases, $V^\text{Th}_\text{stop}$ became further apart as indicated by the larger $a$ to be overcome, thus resulting in a decrease in $n_{\text{Th}}$ while $\phi_T$ remained fairly constant at $0.86$ eV. As a larger $a$ is caused by a less dense filament or lower $n_{\text{Th}}$, the hopping conduction analysis also validates the inverse relationship between $V_{\text{stop}}$ and $n_{\text{Th}}$.

**CONCLUSIONS**

In conclusion, the multilevel resistance states of Pt/HfO$_2$/Ti RRAM devices obtained from increasing $V_{\text{stop}}$ have shown to be directly related to $E_{\text{AC}}$ but inversely related to $n_{\text{Th}}$. The average $E_{\text{AC}}$ value was extracted from an Arrhenius equation to be $0.022$ eV at a wide temperature range of $-40$ to $175$ °C and was shown to be inversely proportional to $n_{\text{Th}}$ as a part of our proposed switching model. The multilevel high resistance states were achieved at $V_{\text{stop}}$ from $-0.9$ to $-1.3$ V at intervals of $-0.1$ V. In the validation of the relationship between $n_{\text{Th}}$ and $V_{\text{stop}}$ kMC simulations exhibited a decrease in $n_{\text{Th}}$ at increasing $V_{\text{stop}}$ at different regions of the filament. The decrease in $n_{\text{Th}}$ at increasing $V_{\text{stop}}$ was also attributed to a larger trap-to-trap distance to be overcome from $0.83$ to $0.93$ nm in the hopping conduction mechanism analysis. The uniformly fabricated Pt/HfO$_2$/Ti devices exhibited at least $5 \times 10^5$ endurance cycles at $100$ ns with a retention for more than $10$ years at $125$ °C. With good thermal stability and multilevel state capabilities, Pt/HfO$_2$/Ti RRAM devices and their proposed models have great potential for neuromorphic engineering in automobiles.

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A1687b0033) for supporting this work.

We acknowledge the RIE2020 ASTAR AME IAF-ICP grant (no. I1801E0030) and ASTAR AME Programmatic Grant (no. A1687b0033).

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. D.J.J.L. conceived the idea and designed this work. D.J.J.L. performed most of the resistive switching device fabrication, characterizations, and analysis of results. D.J.J.L., P.A.D., and S.C.W.C. fabricated the devices, while P.A.D., S.C., and E.H.T. provided guidance and suggestions to this work. P.A.D., and S.C.W.C. fabricated the devices, while P.A.D., S.C., and E.H.T. provided guidance and suggestions to this work.

Funding

This work was supported by the RIE2020 ASTAR AME IAF-ICP Grant (no. I1801E0030) and ASTAR AME Programmatic Grant (no. A1687b0033).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the RIE2020 ASTAR AME IAF-ICP grant (No. I1801E0030) and ASTAR AME Programmatic Grant (no. A1687b0033) for supporting this work.

ABBREVIATIONS

I–V, current–voltage; E_{ac}, activation energy; V_{stop}, RESET stop voltage; V_{ox}, oxygen vacancy; n_{ox}, oxygen vacancy density; HRS, high resistance state; KMC, kinetic Monte Carlo; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; RRAM, resistive random access memory; MIM, metal–insulator–metal; CMOS, complementary metal oxide semiconductor; V_{read} read voltage; PVS, pulsed voltage stress; DFT, density functional theory; n_{fil}, number of oxygen vacancies; FN, Fowler–Nordheim; TAT, trap-assisted tunneling

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