Carrier-transport-path-induced switching parameter fluctuation in oxide-based resistive switching memory

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Abstract
A key challenge in resistive switching memory is to reduce the switching parameter fluctuation, which always affects the stability and reliability of an RS device. Numerous methods have been carried out for improving the fluctuation of the switching parameter. However, because the physical nature of the switching parameter fluctuation is, to date, not well understood, a universal identification of the switching parameter fluctuation still has not be achieved. Based on the activation energy of carrier transport from the first-principles calculations, we present a physical model. This proposed model is considering the macroscopic fluctuating I–V curve and material microstructure to analyze the characteristics of carrier transport and the origin of switching parameter fluctuations. The proposed model may specially identify the defect energy level and quantify the distribution of the switching parameter. The model provides possible clues for improving the uniformity of the switching parameter as well.

1. Introduction
Oxide-based resistive switching memories have received tremendous attention from both academic and industrial communities due to the excellent memory performance [1–5]. The resistance changing behavior in oxide-based resistive switching (RS) memory is widely accepted to relate to the formation and rupture of the conducting filament (CF) [6, 7]. Generally, the percolation of some kinds of defects, such as interstitial defects and oxygen vacancies [8, 9], contributes to the formation of CF. Among several kinds of defects in oxide-based RS memory, oxygen vacancies are considered to dominate the generation of conducting paths and thereby remarkably affect carrier transport properties [10–12]. To clarify how oxygen vacancies influence the transport property, various experimental and theoretical efforts have been employed [13, 14]. In addition, after the formation of CF the carrier transport in oxide-based RS memory is based on hopping between oxygen vacancies, which may be described effectively in terms of activation energy [15, 16]. Numerous theories, such as Monte Carlo and trap-assisted tunneling (TAT) [17, 18], have recently been performed to investigate carrier transport; however, the effect of the oxygen vacancy type and activation energy on the carrier transport has never been addressed.

Since the formation of CF is random and the charge carriers may not move through the same path for every switching cycle [19], the uniformity of switching parameters for each switching cycle will be very poor. For the oxide-based RS memory, a key challenge is to reduce the switching parameter fluctuation which greatly affects the stability and reliability of the RS device [20]. Many methods, such as inserting thin interfacial layers between the switching layer and electrode [21], embedding nanocrystals into the switching layer [22], and doping [23], have been carried out for improving the uniformity of the switching parameter. However, a universal identification of the switching parameter fluctuation could not be achieved, because the physical nature of the switching parameter is still ambiguous. Progress in understanding the physics behind the carrier transport in CF and hence the switching parameter fluctuation is imperative for design of high-performance and reliable devices.
Here, on the basis of the activation energy of carrier transport from the first-principles calculations, we will present a physical model connecting macroscopic fluctuating I–V curve and material microstructure in oxide-based RS memory to investigate the characteristics of carrier transport and the origin of the switching parameter fluctuation. More importantly, we will firstly analyze the effect of activation energy of carrier transport and oxygen vacancy type on the carrier transport in CF. Some guidelines reducing the fluctuation of switching parameter are also provided.

2. Experimental

All measured RS devices (Pt/Ti/HfO$_2$/Pt, Pt/TiN/ZrO$_2$/Pt, Pt/Cu/WO$_3$/Pt) in this work had a dimension of $10 \times 10 \mu$m, which were obtained by standard nanofabrication process. The RS layer (HfO$_2$, ZrO$_2$, WO$_3$) was deposited by atomic layer deposition and the other layers were deposited by sputtering. The schematic structure of the sample is similar as [24].

The current–voltage (I–V) characteristics were carried out by the Keithley 4200-SCS semiconductor characterization system. During all the measurements, the bias voltage was applied on the top electrode while the Pt bottom electrode was grounded.

3. Model

To illustrate the carrier transport in CF and the switching parameter fluctuation, the HfO$_2$-based RS device is firstly used as an example. It is well known that, below 2000 K, hafnia (HfO$_2$) is monoclinic C$2_1$/c phase with space group p2$_1$/c [25] and only includes two types of oxygen vacancies [26, 27], here marked as VO$_3$ and VO$_4$, respectively. Generally speaking, the activation energy can be thought of as the height of the energy barrier. Here it will be shown that the activation energy of carrier transport for each oxygen vacancy, which is defined to be the energy that carrier leaves the defect energy level of oxygen vacancy for the conduction band, can be determined as the energy gained when the electron from the bottom of the conduction band is trapped at the defect as follows [26, 27]

$$E_a = E_p^{-1} + E_D^0 - E_p^0 - E_D^{-1} + \delta,$$

where $E_p^0$ and $E_p^{-1}$ are the total energy of perfect supercell with charge 0 and $-1$, respectively, $E_D^0$ and $E_D^{-1}$ are the energy of defect supercell with charge 0 and $-1$, respectively, $\delta$ is the correction for the position of the conduction band bottom which is equal to the difference between the experimental and calculated band gap. For various oxygen vacancies, the activation energy is different due to the different height of the energy barrier.

To obtain the total energy with a perfect cell and defect cell, we performed the first-principles calculations with the CASTEP code [28]. Since DFT-GGA usually underestimates band gaps [29], in this work the electronic interactions are described within the GGA + $U$ formalism for the HfO$_2$ cell [13]. The total energy of the perfect supercell and defect supercell is calculated with the PW91 version of GGA + $U$, respectively. The detailed calculation process can be found in our previous work [30].

Figure 1 shows the calculated density of states (DOS) for monoclinic HfO$_2$ ($m$-HfO$_2$) phase with perfect and defect cell, respectively. Compared with the DOS of the perfect cell in figure 1(a), the calculated DOS of the defect cell obviously shifts toward the depth energy level, and a new DOS peak has arisen near the Fermi level (see in figures 1(b) and (c)). The results suggest that oxygen vacancy may result in the generation of new DOS in the system, which could well improve the carrier transport properties in oxide-based RS memory. Otherwise, according to the result of first-principles calculations and connecting equation (1), the activation energy of carrier transport in each oxygen vacancy can be calculated, i.e. $E_a = 1.233$ eV in VO$_3$ and $E_a = 1.341$ eV in VO$_4$.

Since the activation energy can be thought of as the height of the energy barrier, the smaller the activation energy, the shallower the energy level of oxygen vacancy, i.e. the energy level of VO$_3$ is shallower than the energy level of VO$_4$.

According to the hopping theory, conduction is the result of many series of hops through hopping space. In this situation, the total resistance of the hopping process in low-resistance state (LRS) or high-resistance state (HRS) is

$$R_{tot} = R_1 + \ldots + R_i + \ldots + R_n,$$

where the subscript $i$ is the carrier hopping of $i$th number of times, $R_i$ is the resistance of the carrier hopping of $i$th number of times, $R_{tot} = \sigma_{tot}^{-1} = \sigma_0^{-1} \exp \left( \frac{qE_a(path)}{k_BT} \right)$, $R_i = \sigma_0^{-1} \exp \left( \frac{qE_a}{k_BT} \right)$, $E_a$ is the conductance pre-factor, $k_B$ is the Boltzmann constant, $T$ is the device temperature, $E_a(path)$ is the average activation energy for
each carrier transport path, \( E_{a(i)} \) is the activation energy of the carrier hopping of \( i \)th number of times, \( \alpha \) is the inverse of localization length, \( R_{ij} \) is the carrier hopping distance.

Equation (2) then reduces to

\[
\exp \left( \frac{qE_{a(path)}}{k_B T} \right) = \exp \left( 2\alpha R_{ij} + \frac{qE_{a(1)}}{k_B T} \right) \ldots + \exp \left( 2\alpha R_{ij} + \frac{qE_{a(n)}}{k_B T} \right)
\]

On the basis of equation (3), one can calculate the average activation energy for all of carrier transport paths for HRS and LRS, respectively.

To identify each defect level of carrier transport and extract the carrier transport path in CF, a key factor is to connect the macroscopic I–V characteristics and material microstructure. According to the calculation flowchart in our previous work [30], the relationship between the macroscopic I–V characteristics and material microstructure is achieved by the average activation energy, that is, the average activation energy \( (E_{a(ave)}) \) in CF and the average activation energy of the carrier transport path \( (E_{a(path)}) \). Next, we will calculate the average activation energy \( (E_{a(ave)}) \) in CF by the following equations (4)–(8).

After the formation of CF in oxide-based RS memory, CF is well recognized to include two states: HRS and LRS. During the operation in LRS the carrier jumps among a series of defect sites. According to the variable range hopping (VRH) theory, the site energy for different defect sites is very different. Therefore the carrier hopping distances should be various, which can lead to different resistance in LRS. The larger the resistance, the lower the probability that carrier transport occurs. The different probability of carrier transport would cause the formation of various carrier transport paths and hence induces the switching parameter fluctuation in oxide-based RS memory. On the other hand, except of a series of defects for HRS, there is a gap in CF, and switching
parameter fluctuation is attributed to both the movement of the carrier through different defects and the distances of the gap.

In LRS, for ohmic contact the electric field distribution is uniform, while in HRS, the electric field distribution obeys Poisson’s equation in hopping progress because of space charge–limited current effect follows as:

$$\frac{dF(x)}{dx} = -\frac{nq}{\varepsilon},$$  \hspace{1cm} (4)

where $n$ is the carrier concentration, $q$ is the electronic charge, $\varepsilon$ is the dielectric permittivity, $F(x)$ is the electric field with the distance $x$ in CF.

The electron current for the hopping process in HRS is calculated by

$$I_{\text{hopping}} = nq\mu_0 \exp\left(-\frac{qE_{\text{a(ave)}}}{k_BT}\right) F(x) S,$$  \hspace{1cm} (5)

where $\mu_0$ is mobility pre-factor, $k_BT$ $E_{\text{a(ave)}}$ is the average activation energy of carrier transport in HRS, $S$ is the cross-sectional area of CF.

According to the theory of Fowler–Nordheim emission, the tunneling current is calculated as [31, 32]

$$I_{\text{tunneling}} = \frac{q^3F_1^2S}{8\pi\hbar m}\exp\left(-\frac{8\pi\sqrt{2m}\left(q_B + E_{\text{a(ave)}}\right)^{3/2}}{3hqF_1}\right),$$  \hspace{1cm} (6)

where $F_1$ is the electric field during tunneling process, $h$ is Planck’s constant, $q_B$ is the barrier height, $m$ is the free electron mass, $E_{\text{a(ave)}}$ is the activation energy of carrier transport in CF. Here, the hopping current is equal to the tunneling current in CF in HRS.

The applied voltage in CF can be written as

$$V = V_{\text{hopping}} + V_{\text{tunneling}} = \int_0^{L_1} F(x) dx + F_1(L - L_1),$$  \hspace{1cm} (7)

where $L$ is the HfO$_2$ thickness, $L_1$ is the length of hopping process.

In LRS, the electron current can be simply written as

$$I = \sigma_{\text{LRS}}F_2S = \sigma_0 VS\left(F_2\right) \exp\left(-\frac{qE_{\text{a(ave)}}}{k_BT}\right),$$  \hspace{1cm} (8)

where $F_2$ is the electric field of LRS in CF, $\sigma_0$ is the conductance pre-factor, $E_{\text{a(ave)}}$ is the average activation energy of carrier transport in LRS.

By using the calculation flowchart as in [30], the experimental $I$–$V$ curve can be simulated, and the current distribution in HRS and LRS can be determined. According to the current distribution, the switching parameter fluctuation is defined as the difference between the maximum and minimum value of current distribution as

$$\Delta I = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}}} \times 100\%,$$  \hspace{1cm} (9)

where $I_{\text{max}}$ and $I_{\text{min}}$ are the maximum and minimum values of current distribution at a constant read voltage, respectively. Here, the smaller the $\Delta I$, the lower the switching parameter fluctuation.

4. Results and discussion

Figure 2(a) shows the simulated and experimental $I$–$V$ curves of the HfO$_2$ device for several sweeps during the set process. The thickness of HfO$_2$ is 5 nm and the measurement temperature is 300 K. Good agreements between the simulated and measured data were observed. The input parameters are $T = 300$ K, $L = 5$ nm, $\alpha = 0.6$ nm$^{-1}$ [33], $R_{ij} = 0.455$ nm, $q_B = 2.48$ eV [34], $\mu_0 = 1 \times 10^{10}$, $\varepsilon = 23$ [35], $\sigma_0 = 5 \times 10^{22}$, $S = 40$ nm$^2$ [36], $E_a = 1.15$ eV (the activation energy of carrier transport for VOD; VOD represents the abbreviation of the other defects excluding the oxygen vacancies). Here, $\mu_0$ and $\sigma_0$ are the mobility pre-factor and conductance pre-factor, respectively, which do not have specific physical significance and are used just for fitting the experimental data. Otherwise, the other defects, such as the interstitial and ion defects, may also contribute to the carrier transport. Therefore, the other defects (VOD) excluding the oxygen vacancy will be included in discussing carrier transport. Based on our previous method [30], one can identify the defect energy level and extract the actual carrier transport path. Figures 2(b)–(d) show the identified defect energy landscape in CF for the different
operated process in figure 2(a). It is clear that the I–V characteristic (figure 2(a)) changes with the sites of different defect energy levels and height of the energy barrier for each defect in CF. In terms of the energy landscape in CF and corresponding defect types, we can easily draw the carrier transport paths for the experimental I–V of different sweeps in figure 2(a), as shown in figure 2(e). Moreover, please note that since the probability of carrier transport is various in different defect energy levels in CF, the charge carriers cannot move through the same path for each switching. As a result, the different carrier transport paths for each switching...
would induce the switching parameter fluctuation in oxide-based RS memory. The switching parameter fluctuation in RRAM could be generally affected by many factors, such as fabrication method, operation mode, etc; however, the most intrinsic effect is attributed to the carrier transport and corresponding path in CF. In this work, we will mainly focus on the effect of the carrier transport path on the switching parameter fluctuation and ignore other factors.

Since the carrier transport path in CF could be affected by the defect energy level, defect type along with concentration, device thickness, temperature and material, next we will discuss the effect of these factors on the switching parameter fluctuations. As pointed out above, oxygen vacancies are dominant to the generation of a conducting path in oxide-based RS memory, so we keep a constant VOD concentration of 10% in the full manuscript. The switching parameter fluctuation would be calculated according to equations (3), (5), (8) and (9); the detailed calculation flowchart has been reported in our previous work [30].

Figure 3(a) shows $\Delta I$ as a function of the activation energy of carrier transport ($E_a$) in VOD. The input parameters are the same as those in figure 2. One can see that, when the activation energy of the carrier transport in VOD is between 1.233 eV and 1.341 eV, $\Delta I$ keeps a constant minimum value for HRS and LRS, respectively. The results indicate that the switching parameter fluctuation has the lowest value, as the activation energy of carrier transport in VOD is in the range of 1.233–1.341 eV. When $E_a$ in VOD is lower than 1.233 eV or larger than 1.341 eV, $\Delta I$ will increase and gradually trend to a constant, and the switching parameter fluctuation thus also increases with the changing $E_a$ in VOD. Generally, the probability of carrier transport is much larger in the shallower energy level than in the deeper energy level. In addition, as mentioned above, the larger the $E_a$ for VOD, the deeper the VOD defect level. When the VOD defect energy level is enough deep, for example, when $E_a$ in VOD is larger than 1.341 eV, carriers only jump via hopping between oxygen vacancies and cannot jump in VOD, thus the switching parameter fluctuation is attributed to the oxygen vacancy and $\Delta I$ trends to a constant.

In contrast, when $E_a$ for VOD is lower than 1.233 eV, the probability of carrier transport in VOD will increase, at which the switching parameter fluctuation is attributed to both oxygen vacancy and VOD defect. Therefore $\Delta I$ increases with decreasing the $E_a$ in VOD. As a result, in the process of preparing the RS devices, if one can take effective methods to control the VOD defect energy level, the switching parameter fluctuation could be reduced.

Figure 3. The effect on switching parameter fluctuation of (a) activation energy of carrier transport in VOD, (b) oxygen vacancy concentration, (c) temperature and (d) device thickness.
Figure 3(b) shows the oxygen vacancy concentration dependence of $\Delta I$. The input parameters are the same as those in figure 2. It is found that increasing VO3 or decreasing VO4 concentration may remarkably reduce $\Delta I$, which suggests that the increase of VO3 concentration or decrease of VO4 concentration may improve the switching parameter fluctuations. The reason is that the VO3 defect energy level is shallower than the VO4 defect energy level, and increasing VO3 or decreasing VO4 concentration means to enhance the ratio of the shallower energy level. The switching parameter fluctuation could be reduced with increasing the probability of carrier transport in the shallower energy level, as the probability of carrier transport is larger in the shallower energy level than that in the deeper energy level.

Figure 3(c) shows the comparison between the calculation and experimental data for temperature dependence of $\Delta I$ in HRS and LRS, respectively. The input parameters are: $L = 5$ nm, $E_a = 1.261$ eV (VOD); the VO3 concentration is 20%; and the other parameters are the same as those in figure 2. It is clear here that $\Delta I$ decreases with temperature increasing, which indicates that the increase of temperature may improve the switching parameter fluctuation. Because carriers in deeper states can jump to shallower states by thermal excitation, increasing temperature can increase the carrier thermal excitation rate and decrease the height of the energy barrier of carrier transport. Consequently, the switching parameter fluctuation will reduce with the increase in the temperature. The agreement between the experimental and calculated results is good.

Figure 3(d) shows the comparison between the calculation and experimental data for thickness dependence of $\Delta I$ in the HfO2 RS device for HRS and LRS, respectively. The input parameters are $E_a = 1.27$ eV (VOD), VO3 concentration is 20%, and the other parameters are the same as those in figure 2. One can see that $\Delta I$ increases with the increase in HfO2 thickness. The results suggest that the increase in device thickness could enlarge the switching parameter fluctuation. The reason is that increasing device thickness may increase the distance of carrier transport and the amount of defect, and hence the paths of carrier transport for each switching. As a result, the switching parameter fluctuation increases with the increase in device thickness. The calculated results well agree with the experimental data.

Finally, we want to discuss the effect of material on the switching parameter fluctuation in RS memory. Here, three RS materials, i.e. HfO2, ZrO2 and WO3, will be chosen as the samples. In addition, to clearly reveal the influence of the material, we only investigate the effect of oxygen vacancy and ignore the other defects. We firstly calculate the defect energy levels of oxygen vacancies and activation energy for different materials based on the first-principles calculations as mentioned above. Figure 4 shows the schematic illustration of the calculated defect energy levels associated to the different oxygen vacancy of HfO2, ZrO2 and WO3, respectively. The difference of activation energy ($\Delta E_a$) between maximum and minimum defect level ($\Delta E_a = E_{a,\text{max}} - E_{a,\text{min}}$).
(8), and connecting equation (9), $\Delta I$ in HRS and LRS can be calculated, respectively. The input parameters are as follows: for the HfO$_2$ device, $L = 10$ nm, the other parameters are the same as those in figure 2; for ZrO$_2$ device, $\alpha = 0.69$ nm$^{-1}$, $R_{ij} = 1$ nm, $\varphi_B = 2$ eV [36], $\mu_0 = 2.2 \times 10^5$, $L = 10$ nm, $\epsilon = 25$, $\sigma_0 = 10^{13}$, $S = 40$ nm$^2$, $E_a = 2.15$ eV (VOD); and for WO$_3$ device, $\alpha = 1.1$ nm$^{-1}$, $R_{ij} = 1$ nm, $\varphi_B = 1.19$ eV [37], $\mu_0 = 2.2 \times 10^5$, $L = 10$ nm, $\epsilon = 35.2$, $\sigma_0 = 10^{13}$, $S = 40$ nm$^2$, $E_a = 0.79$ eV (VOD). In order to verify the theoretical results, we also measured current distributions for the HfO$_2$, ZrO$_2$, and WO$_3$ devices at a read voltage of 0.1 V, respectively, as shown in figure 5.

Table 1. Comparison of the difference of activation energy ($\Delta E_a$) and $\Delta I$ for the RS device with different materials.

| Material | HfO$_2$ | ZrO$_2$ | WO$_3$ |
|----------|---------|---------|--------|
| $\Delta E_a$ (eV) | 0.108 | 0.091 | 0.150 |
| $\Delta I$ in HRS (Simulation) | 72.65% | 69.11% | 89.74% |
| $\Delta I$ in HRS (Experiment) | 73.53% | 69.00% | 93.11% |
| $\Delta I$ in LRS (Simulation) | 85.82% | 82.85% | 91.21% |
| $\Delta I$ in LRS (Experiment) | 84.36% | 80.62% | 94.37% |

Figure 5. Measured current distributions of 100 repetitive I–V sweeps at read voltage of 0.1 V and $\Delta I$ calculated by equation (9) in LRS and HRS: (a) HfO$_2$, (b) ZrO$_2$, and (c) WO$_3$.
Therefore, ZrO$_2$ RS device displays the best uniformity of switching parameter, as compared with HfO$_2$ and WO$_3$ RS device. The calculated results agree well with the experimental data, as shown in table 1.

5. Conclusion

In summary, based on the activation energy of carrier transport from the first-principles calculations a physical model connecting macroscopic fluctuating I–V characteristics and material microstructure was proposed to analyze the defect energy level of conducting filament in oxide-based RS memory. The proposed model may specially identify the defect energy level and quantify the distribution of switching parameter. According to the proposed model, some possible clues for improving the uniformity of switching parameter have been provided: (1) controlling the VOD defect level by some effective fabrication methods, (2) increasing VOS or decreasing VO4 concentration, (3) increasing temperature, (4) decreasing device thickness, and (5) choosing the material with lower $\Delta E_m$.

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