AIP Applied Physics Letters

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Citation: Applied Physics Letters **104**, 052108 (2014); doi: 10.1063/1.4864471
View online: http://dx.doi.org/10.1063/1.4864471
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/5?ver=pdfcov
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APPLIED PHYSICS LETTERS **104**, 052108 (2014)

Tunnel barrier engineering of titanium oxide for high non-linearity of selector-less resistive random access memory

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(Received 19 December 2013; accepted 25 January 2014; published online 7 February 2014)

In this study, the effect of the oxygen profile and thickness of multiple-layers TiO_x on tunnel barrier characteristics was investigated to achieve high non-linearity in low-resistance state current (I_{LRS}). To form the tunnel barrier in multiple-layer of TiO_x, tunnel barrier engineering in terms of the thickness and oxygen profile was attempted using deposition and thermal oxidation times. It modified the defect distribution of the tunnel barrier for effective suppression of I_{LRS} at off-state ($^1/_2V_{Read}$). By inserting modified tunnel barrier in resistive random access memory, a high non-linear I_{LRS} was exhibited with a significantly lowered I_{LRS} for $^1/_2V_{Read}$. *© 2014 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4864471]

Resistive random access memories (ReRAMs) have been considered next-generation non-volatile memories, capable of solving the scaling limit problem of conventional flash memory.[1–4] ReRAM is a simple structure with a two terminals, and its high-density cross-point array is expected to be able to replace Flash memory.

However, the sneak path current which is the interference from neighboring cells can degrade the readout margin of a high density cross-point array. This sneak path current is caused by a high low-resistance state current (I_{LRS}) at the off-state ($^1/_2V_{Read}$). Current can flow to the low-resistance state (R_{LRS}) cell during the reading operation for high-resistance state (R_{HRS}) cell. To suppress the sneak path current, various selector devices—metal insulator transition (MIT), ovnonic threshold switching (OTS), mixed ionic-electronic conductors, and exponential switching—have been investigated.[5–8] In case of MIT devices, it still retains high operating current for its selectivity. The exponential selector devices have significantly low operating current for high-density cross-point array applications with low sneak-path current. But, they exhibit also low current at on-state for I_{LRS} of ReRAM. They cannot satisfy operating current (I) and voltage (V) of ReRAM for 1selector and 1ReRAM (1S1R). In case of OTS, it has very complicated materials composition for its reliable operation. In addition, these selector devices can increase the number of stacked layers in 1S1R devices fabrication. Furthermore, selector devices have required operating I–V matching with ReRAM operating range. To overcome the problems of 1S1R integration and operating I–V range, selector-less ReRAMs with non-linear characteristics have been investigated.[9–12] It requires very simple structure of its reliable operations. The simple structure of ReRAM devices can lead reliable operation with high yield in wafer level fabrication. Although non-linear ReRAMs have an advantage of its simple structure, their non-linearity values are still insufficient, and the origin of the non-linearity was not deeply investigated. However, TiO_x has been reported to exhibit the non-linear I_{LRS} with thermally formed sub-oxide TiO_x by high compliance current.[9] It obtained the non-linear I_{LRS} of TiO_x by using the method of thermally activated energy.

In this study, tunnel barrier engineering of multiple-layers of TiO_x was investigated as a method to achieve the high non-linear I_{LRS}. We had controlled thickness and the oxygen profile of TiO_x tunnel barrier for high non-linearity. Optimum thickness and the oxygen profile of tunnel barrier can effectively reduce electron transfer at low voltage level with direct tunneling suppression, whereas this tunnel barrier can exhibit high current flowing at high voltage level with its Fowler–Nordheim (FN) tunneling of barrier lowering. Therefore, tunnel barrier engineering could be used to modify the defect distribution of the tunnel barrier to achieve high non-linearity and suppress I_{LRS} at $^1/_2V_{Read}$. Compared to a typical linear ReRAM, we could obtain the sufficient I_{LRS} at on-state (V_{Read}), whereas the I_{LRS} at $^1/_2V_{Read}$ could be significantly reduced by the highly non-linear tunnel barrier characteristics.

We fabricated $Pt/Ti/HfO_2/TiO_x/Pt$ devices in a 250-nm via-hole structure. For the isolation layer, a 100-nm thick SiO_2 sidewall layer was deposited on a $Pt/Ti/SiO_2/Si$ substrate using plasma-enhanced chemical vapor deposition. Subsequently, a 250-nm via-hole was defined using the conventional KrF lithography process, followed by reactive ion etching. First, a 6-nm-thick layer of TiO_x was deposited for a tunnel barrier in an Ar and O_2 mixed plasma using RF sputtering. To form the multiple-layers of TiO_x, TiO_x layer was annealed in an oxygen ambient by using rapid thermal annealing at 300 °C. This could oxidize the top surface of the TiO_x layer, which formed a TiO_y ($y > x$) layer at the top surface of the TiO_x. A 4-nm-thick HfO_2 layer was deposited using an atomic layer deposition system to form the main switching layer, using tetrakis(ethylmethylamino)hafnium (TEMAH) as a precursor and H_2O as an oxidizer at 250 °C. The Ti oxygen reservoir and Pt top electrode (TE) were deposited using DC sputtering and defined using a 50 μm shadow mask (Figure 1).

The gray line of Figure 2(a) shows the DC I–V curve, which indicates the linear characteristics of the typical ReRAM (TE/Ti/HfO_2/BE). A DC bias was applied to the

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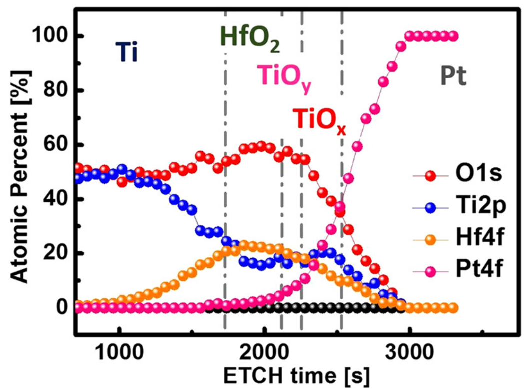

FIG. 1. XPS depth profile of selector-less ReRAM with $Pt/Ti/HfO_2/TiO_x/Pt$ stacks. The multiple-layers TiO_x tunnel barrier was observed.

TE, and the bottom electrode (BE) was grounded. The resistance changed from R_{HRS} to R_{LRS} with conductive filament when positive bias was applied to the TE. In contrast, the resistance changed from R_{LRS} to R_{HRS} with filament dissolution when negative bias was applied to the TE. Typical ReRAM switching is attributed to filament formation and dissolution at HfO_2 main switching layer. This linear ReRAM has high I_{LRS} at $1/2V_{Read}$, it degrades readout margin at cross-point array operation. To lower I_{LRS} at $1/2V_{Read}$, TiO_x tunnel barrier was inserted between main switching layer and BE.

Figure 2(a) shows the DC I–V curve of the high non-linear characteristics of the selector-less ReRAM ($TE/Ti/HfO_2/TiO_x/BE$) with a $50\,\mu A$ compliance current. Non-linearity is defined using[9]

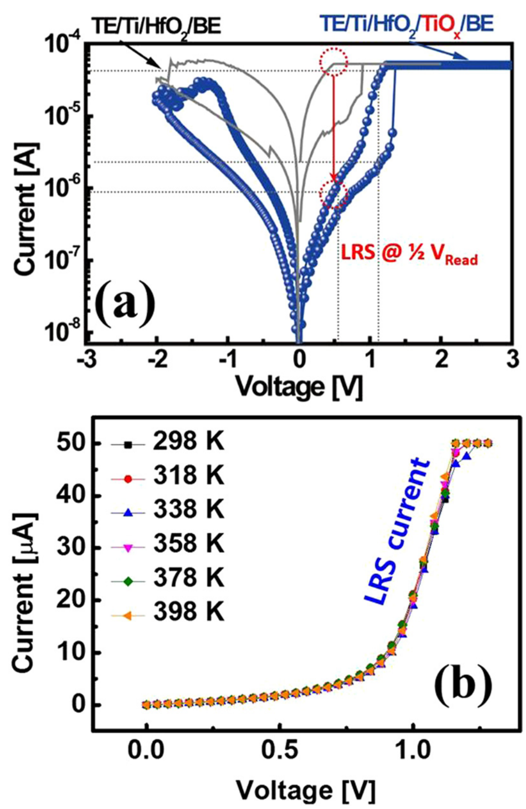

FIG. 2. (a) Typical high non-linear DC I–V switching characteristics of the selector-less ReRAM with comparison of the linear ReRAM. (b) I_{LRS} temperature independence behavior of the selector-less ReRAM with thermal stability.

$$\text{Non-linearity} = (I\,@\,V_{set})/(I\,@_{1/2}V_{set}). \tag{1}$$

Compared with a typical linear ReRAM, the tunnel barrier engineered $TE/Ti/HfO_2/TiO_x/BE$ structure exhibited a substantially lowered I_{LRS} at $1/2V_{Read}$ owing to its highly non-linear behavior. Hence, it can be applicable for cross-point array implementation without any selectors because of the high non-linearity. Figure 2(b) shows the thermal stability of the selector-less ReRAM up to 398 K. Based on this temperature independence behavior, we could confirm that the non-linearity originated with the tunnel barrier characteristics. Tunnel barriers are well known to exhibit temperatures that are not dependent on the non-linear I–V characteristics with direct and FN tunneling mechanisms as a results of the barrier height modification. Once a filament is formed in HfO_2, the HfO_2 of the main switching layer can assume an ohmic state for the conductive filament, and the barrier height modification of the tunnel barrier mainly controls the non-linear I_{LRS} behavior. Thus, we have to consider the non-linear I–V behavior in relation to the tunnel barrier characteristics.

Hence, tunnel barrier engineering in terms of the TiO_x thickness and oxygen profile control had been investigated because these characteristics modulate tunnel barrier properties in order to obtain high non-linearity in a selector-less ReRAM, as shown in Figures 3(a) and 3(c).[13,14] First, we could suppress the electron transfer at $1/2V_{Read}$ along the tunnel barrier by using the optimum thickness of a tunnel barrier. However, if the tunnel barrier was too thick, it could not exhibit sufficient I_{LRS} at V_{Read} because the electron transfer was even too suppressed in high voltage level. By contrast, if the tunnel barrier was too thin, most electric field can be applied to the tunnel barrier, and high I_{LRS} can flow. It is well known that high electric field can degrade oxide reliability. It results in poor endurance reliability of ReRAM. Hence, too thick or too thin tunnel barrier could decrease the non-linearity and its yield. Thus, it was found that a 6-nm-thick TiO_x tunnel barrier exhibited the highest non-linearity (Figures 3(a) and 3(b)). Next, we controlled the oxygen profile of the 6-nm TiO_x tunnel barrier to achieve higher non-linearity with thermal oxidation at 300 °C (Figures 3(c) and 3(d)). Thermal oxidation could elaborately oxidize the top surface of a TiO_x tunnel barrier to form a more insulating state. Thus, it could precisely determine the thickness of the oxidized layer on the top surface with thermal oxidation time. Hereafter, we define the top surface of the insulating TiO_x as TiO_y ($y > x$). By adopting the multi-layer TiO_y/TiO_x, the TiO_x thickness was decreased to 3.5-nm with 2.5-nm of TiO_y (Figure 4(a)). Energy-dispersive X-ray spectroscopy (EDX) shows that the top surface of TiO_x tunnel barrier has more oxygen content than the TiO_x bulk region. Hence, the single state TiO_x was changed to the multi-layer TiO_y/TiO_x, which contained an insulating top surface and a relatively metallic bulk region. The existence of this multi-layer TiO_y/TiO_x was also confirmed using an X-ray photoelectron spectroscopy (XPS) binding energy analysis of the TiO_x layer (Figures 4(b) and 4(c)).[15] Consequently, dominant peak of Ti^{4+}, which related to the insulating state was obtained at the top surface of TiO_x tunnel barrier, and Ti^{2+} as the relatively metallic state TiO_x

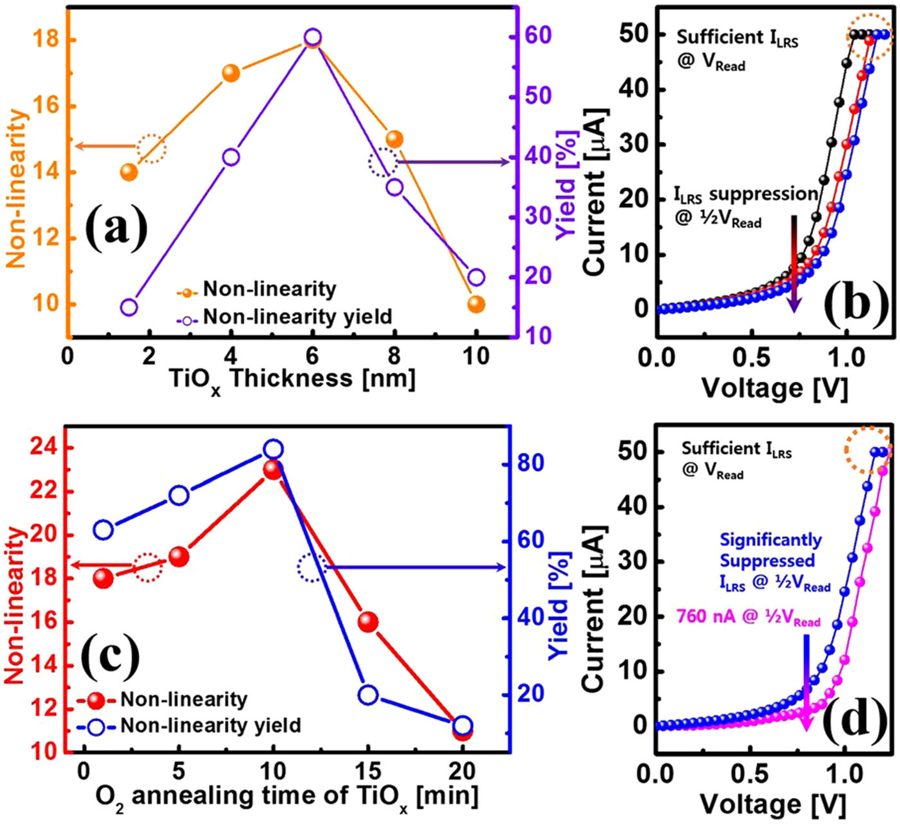

FIG. 3. (a) Non-linearity and yield improvement up to critical thickness of TiO_x tunnel barrier. (b) More suppressed I_{LRS} at $^1/_2$ V_{Read} and sufficient I_{LRS} at V_{Read}. (c) Oxygen profile dependence of non-linearity and yield. (d) Significantly suppressed I_{LRS} at $^1/_2$ V_{Read} with sufficient on-state I_{LRS}.

tunnel barrier was observed in the bulk region. Modulated TiO_x tunnel barrier exhibited a higher non-linearity and yield with multi-layer TiO_y/TiO_x by using 10 min of thermal oxidation. This tunnel barrier engineered multi-layer TiO_y/TiO_x could directly modify the defect distribution of the tunnel barrier which in turn affected the non-linearity and yield of the selector-less ReRAM (Figure 5). As shown in Figure 5, the multi-layer TiO_y/TiO_x tunnel barrier attributes the high non-linear I–V characteristics with direct and FN tunneling mechanisms. In the multi-layer TiO_y/TiO_x tunnel barrier, the TiO_y and TiO_x layers play an important role for the direct tunneling suppression at low voltage level. TiO_y can suppress direct tunneling owing to its insulating state.

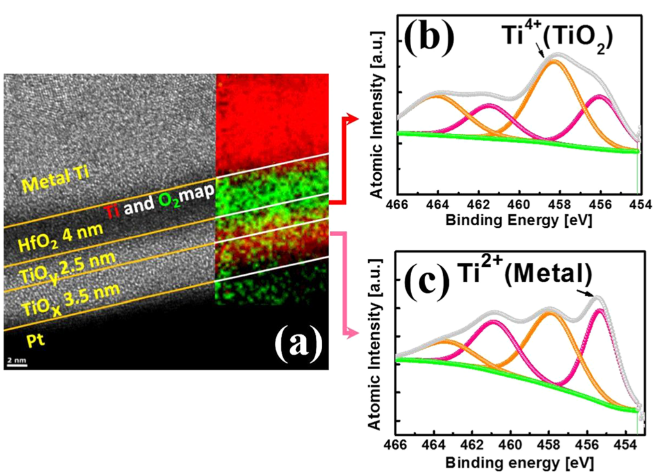

FIG. 4. (a) TEM image with oxygen and Ti distribution of EDX analysis. (b) XPS binding energy analysis for TiO_x tunnel barrier of the top surface. (c) XPS binding energy analysis for TiOx tunnel barrier of the bulk region.

Furthermore, TiO_x assists to suppress electron transfer for lower current flowing at low voltage level because the thicker multi-layer TiO_y/TiO_x can reduce direct tunneling than the thin single layer TiO_y. In high voltage level, TiO_x plays an important role in high I_{LRS}. If we applied high positive bias, the TiO_y region is lowered, and FN tunneling occurred at the TiO_x layer. By contrast, the TiO_x region is lowered, and FN tunneling occurred at the TiO_y layer at high negative bias. In FN tunneling operation of the multi-layer TiO_y/TiO_x, the relatively metallic TiO_x can flow higher I_{LRS} than the relatively insulating TiO_y layer. As shown in the blue curve of Figure 2(a), the I_{LRS} of the positive and negative polarities are different owing to different FN tunneling of TiO_x and TiO_y at high voltage level, respectively. Hence, the both optimum TiO_y (2.5-nm) and TiO_x (3.5-nm) play very important roles in the high non-linear I_{LRS} with effectively suppressed direct tunneling and sufficient FN tunneling. The non-linearity is defined with I_{LRS} ratio at V_{Set} and $^1/_2V_{Set}$. Thus, the multi-layer TiO_y/TiO_x which has both insulating and metallic states is necessary for the high non-linearity and reliability of the selector-less ReRAM.

Consequently, the multi-layer TiO_y/TiO_x could effectively suppress electron transfer at a low voltage level of $^1/_2V_{Read}$ without any cell selector device by high non-linear characteristics of I_{LRS}. In contrast, high voltage level for V_{Read} could sufficiently lower the height of the modified tunnel barrier, and electrons could transfer to the conducting HfO_2 filament region by FN tunneling. By achieving reliable tunnel barrier characteristics, we could retain a sufficient I_{LRS} at V_{Read}, whereas the I_{LRS} at $^1/_2V_{Read}$ could be significantly reduced by the highly non-linear tunnel barrier characteristics. Compared to the typical linear ReRAM, the selector-less ReRAM with the multi-layer TiO_y/TiO_x tunnel

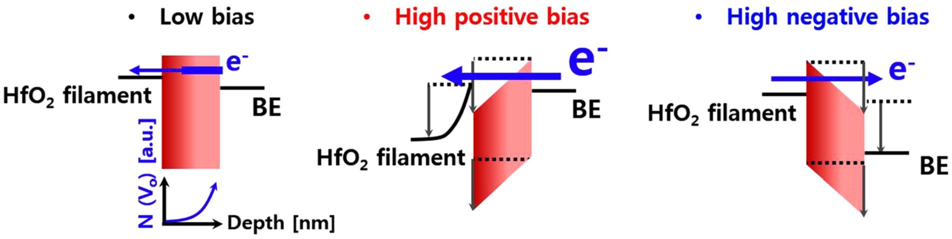

FIG. 5. Tunnel barrier height modification with applying bias and polarity. In off-state, insulating TiO_y and metallic TiO_x effectively suppress electron transfer to reduce I_{LRS}. In on-state, the lowered region of tunnel barrier can be different with applying bias polarity.

barrier exhibited excellent non-linear I_{LRS} without any cell selector device.

This research demonstrated the selector-less ReRAM (∼10 nm thickness) with high non-linearity by the tunnel barrier engineering of the multi-layer TiO_y/TiO_x. The multi-layer TiO_y/TiO_x tunnel barrier plays a very important role in high non-linearity by the suppressed direct tunneling and sufficient FN tunneling. It could reduce I_{LRS} at off-state significantly compared with the typical linear ReRAM without degradation on-state I_{LRS}. Furthermore, It shows a promise for future high density cross-point memory applications.

This work was supported by the R&D MOTIE/KEIT (10039191) and SK Hynix semiconductor.

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