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In this study, the effect of the oxygen profile and thickness of multiple-layers TiOx 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 TiOx, 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 (\(1/2V_{\text{Read}}\)). 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 \(1/2V_{\text{Read}}\). © 2014 AIP Publishing LLC.

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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 (\(1/2V_{\text{Read}}\)). 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 I–V range, selector-less ReRAMs with high non-linearity and suppress I_{LRS} at \(1/2V_{\text{Read}}\). Compared to a typical linear ReRAM, we could obtain the sufficient I_{LRS} at on-state (V_{\text{Read}}), whereas the I_{LRS} at \(1/2V_{\text{Read}}\) 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_{x} (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_{2}O 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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Non-linearity = \left( \frac{I \left( \frac{V_{\text{set}}}{2} \right)}{I \left( \frac{V_{\text{set}}}{2} \right)} \right).

Compared with a typical linear ReRAM, the tunnel barrier engineered TE/Ti/HfO2/TiOx/BE structure exhibited a substantially lowered I_{\text{LRS}} at \frac{1}{2} V_{\text{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 result of the barrier height modification. Once a filament is formed in HfO2, the HfO2 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_{\text{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 TiOx 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). First, we could suppress the electron transfer at \frac{1}{2} V_{\text{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_{\text{LRS}} at V_{\text{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_{\text{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 TiOx tunnel barrier exhibited the highest non-linearity (Figures 3(a) and 3(b)). Next, we controlled the oxygen profile of the 6-nm TiOx 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 TiOx 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 TiOx as TiOx (y > x). By adopting the multi-layer TiOy/TiOx, the TiOx thickness was decreased to 3.5-nm with 2.5-nm of TiOx (Figure 4(a)). Energy-dispersive X-ray spectroscopy (EDX) shows that the top surface of TiOx tunnel barrier has more oxygen content than the TiOx bulk region. Hence, the single state TiOx was changed to the multi-layer TiOy/TiOx, which contained an insulating top surface and a relatively metallic bulk region. The existence of this multi-layer TiOy/TiOx was also confirmed using an X-ray photoelectron spectroscopy (XPS) binding energy analysis of the TiOx layer (Figures 4(b) and 4(c)). Consequently, dominant peak of Ti4+1, which related to the insulating state was obtained at the top surface of TiOx tunnel barrier, and Ti2+ as the relatively metallic state TiOx.
tunnel barrier was observed in the bulk region. Modulated TiOₓ tunnel barrier exhibited a higher non-linearity and yield with multi-layer TiOₓ/TiOᵧ by using 10 min of thermal oxidation. This tunnel barrier engineered multi-layer TiOₓ/TiOᵧ 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 TiOₓ/TiOᵧ tunnel barrier attributes the high non-linear I–V characteristics with direct and FN tunneling mechanisms. In the multi-layer TiOₓ/TiOᵧ tunnel barrier, the TiOᵧ and TiOₓ layers play an important role for the direct tunneling suppression at low voltage level. TiOᵧ can suppress direct tunneling owing to its insulating state. Furthermore, TiOₓ assists to suppress electron transfer for lower current flowing at low voltage level because the thicker multi-layer TiOₓ/TiOᵧ can reduce direct tunneling than the thin single layer TiOᵧ. In high voltage level, TiOₓ plays an important role in high I_LRS. If we applied high positive bias, the TiOₓ region is lowered, and FN tunneling occurred at the TiOₓ layer. By contrast, the TiOᵧ region is lowered, and FN tunneling occurred at the TiOᵧ layer at high negative bias. In FN tunneling operation of the multi-layer TiOₓ/TiOᵧ, the relatively metallic TiOₓ can flow higher I_LRS than the relatively insulating TiOᵧ 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 TiOᵧ and TiOₓ at high voltage level, respectively. Hence, the both optimum TiOᵧ (2.5-nm) and TiOₓ (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_READ. Thus, the multi-layer TiOₓ/TiOᵧ 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 TiOₓ/TiOᵧ 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 HfO₂ 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 TiOₓ/TiOᵧ tunnel
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.

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