Electrical evidence of unstable anodic interface in Ru/HfOₓ/TiN unipolar resistive memory

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Unipolar resistive switching behaviors of Ru/HfOₓ/TiN devices with Ru as anode were investigated. Wide dispersion of switching operation parameters was observed. The conduction mechanisms in low and high resistance states of the devices were characterized to be Ohmic-like and tunneling, respectively. The band offset of the Ru/HfOₓ interface was extracted from the measured tunneling current versus voltage characteristics. Instability of the band offset at the anodic interface was observed and may be responsible for the wide fluctuation of the operation voltage in the Ru/HfOₓ/TiN device at a high resistance state. The possible mechanism for these unstable characteristics of band offset at the Ru/HfOₓ interface is also discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908928]

Transition metal oxide (TMO) based resistive memory with unipolar operation is considered to be a promising candidate for the next generation nonvolatile memory.¹ Through the elucidation of carrier transport in the memory device, several mechanisms were proposed to explain the bistable switching behavior in TMO.²,³ Among the TMO, such as TiO₂ and NiO, the filaments formed in the insulator by the forming process can well describe the transition between the high resistive state (HRS) and the low resistive state (LRS) by the rupture and recovery of the conductive paths.² The anode played a crucial role in maintaining a repetitive resistive switch with unipolar operation.²,³ Kim et al.² reported that most parts of the filaments remain conductive during the switching and only a thin section of the TiO₂ layer near the anode is responsible for the switching. By analyzing the current transport, the thickness of this layer was estimated to be about 3–10 nm by the same group.⁵ However, the exact mechanism of the carrier transport for the resistive memory is still not clear and needs further studies. This is especially true for the TMO based resistive memory, which suffered from the wide dispersion of the operation parameters.⁶ The origin of this unstable switching characteristics needs to be investigated.

In this letter, we studied the unipolar resistance switching properties of the HfOₓ based resistive memory. Although the use of noble metals as anode can lead to an acceptable switching behavior,⁷ still the process integration issues limited their applications in the silicon based memory. Hence, it is necessary to search a metal that is compatible with the silicon process and has an adequate switching behavior. Since ruthenium (Ru) can be easily etched by the O₂/Cl₂ plasma,⁸ thus, Ru was chosen as the anode metal here. To understand the role of the anode/oxide interface during the resistance switching cycle, the current transport characteristics of both the HRS and the LRS for each resistance switching cycle in the Ru/HfOₓ/TiN resistive memory were studied. The effect of band offset at the anodic interface during resistive switching on the dispersive Vₛₑₜ was discussed.

To fabricate Ru/HfOₓ/TiN resistive memories, a 20 nm HfOₓ film was deposited on TiN by atomic layer deposition. The characteristics of the deposited HfOₓ films have been published elsewhere.⁹ A 10 nm Ru film followed by 80 nm TiN capping layer to avoid the oxidation of Ru was deposited by sputtering as the top electrode. The standard lithography and the reactive ion etching were adopted to fabricate the memory cell, which has a square pattern with side ranging from 65 to 640 μm. The electrical properties of the memory device were measured by HP 4155A with the biased Ru anode and the grounded TiN cathode.

The representative I-V curves of the Ru/HfOₓ/TiN resistive memory after the forming process (~5 V) were shown in Fig. 1(a), and the figure inset shows the evolution of the operation voltage for the first 50 resistance switching cycles. In these figures, the wide fluctuation in the resistive switching voltage can be clearly observed. All resistive switching parameters, including the resistance ratio between HRS and LRS (Rₓₕᵢₙɡ/Rₓₙₙ₉₉), Vₛₑₜ, and Vᵣₑₜₑₛₑₙ, show a similar wide dispersion during the switching cycles. The distributions of the Vₛₑₜ and the Vᵣₑₜₑₛₑₙ were shown in Fig. 1(b). The Vᵣₑₜₑₛₑₙ is stable and has a narrow voltage distribution between 1 and 1.3 V. However, the Vₛₑₜ is unstable and shows wide a voltage fluctuation between 2 and 3.5 V. These observations were similar to those of other resistive memory devices with a unipolar operation mode.⁸

Current transport mechanisms for the LRS and the HRS were analyzed by measuring the I-V curve at the temperature ranging from 25 to 180 °C. For the LRS, the I-V curve follows Ohm’s law and the resistivity of the HfOₓ shows a slightly negative temperature dependence (not shown here). Metallic filaments in HfOₓ induced by the set process may be responsible for this observation.¹⁰ On the other hand, the I-V curve of the HRS, as shown in Fig. 2(a), has a positive and weak temperature dependence at low bias. This positive temperature dependence for the HRS current suggests that the dominant current transport mechanism for the devices during
the set process may be tunneling, Schottky emission, or Pool–Frenkel emission. However, we ruled out Schottky emission and Pool–Frenkel emission as possible candidates due to the very weak temperature dependence of the HRS current. From the inset of Fig. 2(a), the HRS current shows a $T^2$ dependence, and this result suggests that the tunneling current is the dominant current transport mechanism in the Ru/HfO$_x$/TiN at low bias. At room temperature, the $J$/$V^2$ vs $1/V$ curve is presented in Fig. 2(b). The linear line with a negative slope at the large bias region of the plot shows that the HRS current at large bias is due to the Fowler–Nordheim (FN) tunneling.

The tunneling current behavior of HRS in the Ru/HfO$_x$/TiN devices suggests that there exists a thin potential barrier to block the current transport. However, the physical thickness of the as-deposited HfO$_x$ film was about 20 nm, which is simply too thick for direct tunneling. According to Ref. 6, the resistance switch of the unipolar resistive memory is located within a thin section of the oxide layer under the anode. Similarly, the scenario for the resistive switching in the Ru/HfO$_x$/TiN can be described as follows: the conductive path is created and the potential barrier of the as-deposited insulator is destroyed during the forming process. An Ohmic current-voltage behavior is observed for the devices. As the device was switched back to the HRS, a thin potential barrier layer near the anode is recovered by the partial rupture of filaments near the anode/HfO$_x$ interface.

The schematic view of the energy band diagram before and after the forming process is shown in the inset of Fig. 2(b).

According to Zafar, when the dominant current transport mechanism of the capacitor device is tunneling, the conduction band offset (CBO) between the oxide and the anode can be extracted from the maximum of the $d(\ln I)/dV$ vs $V$ curve. Figure 3(a) shows the plot of $d(\ln I)/dV$ vs $V$ for the HRS in the given cycle. The extracted CBO between the thin potential barrier of HRS and the anode was found to be 1.7 eV. From the literature, the electron affinity of HfO$_2$ is 2.9 eV; thus, the corresponding work function of Ru was found to be 4.6 eV, which is very close to the reported value of 4.55 eV. The variations in the Ru anode/HfO$_2$ interface during the resistance switching cycles were also studied. The $d(\ln I)/dV$ vs $V$ plot of three typical resistance switching cycles was presented in Fig. 3(b). The statistics of CBO of 50 resistance switching cycles is shown in the inset of Fig. 3(b). As shown in these figures, the CBO varies between 1.1 and 2.3 eV during resistance switching cycles, and the corresponding work function of the anode (assuming a very thin potential barrier for HfO$_2$) varies between 4 and 5.2 eV. It is evident that the anode/oxide interface for this device is highly unstable at HRS.

The work function of the Ru in the Ru/HfO$_2$ system was found to be strongly influenced by the oxygen concentration at the metal oxide interface. Interfaces with deficiency in
oxygen atoms result in the lowering of work function for Ru, while interfaces with excess oxygen concentration lead to the increase of work function for Ru. For the TiO$_2$ resistive memory, the migration of oxygen ion in TiO$_2$ toward the oxide/anode interface is responsible for the resistive switching of the device with unipolar operation. A decrease in the oxygen concentration at the oxide/anode interface was reported. Hence, the variations in the CBO for the Ru/HfO$_x$ interface may be attributed to the variation in the oxygen concentration at the Ru/HfO$_x$ interface during the switching cycles.

By using Zafar's method, the CBO can be found from the transition voltage between the direct tunneling to the FN tunneling. When the device is operated in the FN tunneling region, the current rapidly rises and leads to the final breakdown of the insulator. Therefore, it is expected that there is a linear correlation between the CBO in HRS and the $V_{\text{set}}$. A linear band-shape dependence between the CBO and the $V_{\text{set}}$ can be clearly seen in Fig. 4. This linear band relation suggested that other factors might also influence the $V_{\text{set}}$. As described in last paragraph, during each cycle, the fluctuation in the transport of oxygen ions in the oxide layer leads to the fluctuation in the CBO at the anodic Ru/HfO$_x$ interface during each cycle, as well as the dispersion of $V_{\text{set}}$.

In summary, a repetitive unipolar resistive switching of the memory with the Ru anode was fabricated. The carrier injection in the devices at HRS is governed by the direct tunneling at low bias and the FN tunneling at high bias. The direct tunneling in the device after the reset process suggests that a thin potential barrier layer is recovered at the region near the Ru anode. The variation in the oxygen concentration at the Ru/HfO$_x$ interface during the switching cycles may be responsible for the unstable barrier height at the anodic Ru/HfO$_x$ interface and wide $V_{\text{set}}$ dispersion. For the realization of the Ru/HfO/TiN resistive memory, the oxidation and reduction behaviors of oxygen atoms in HfO$_x$ in the proximity of the anode interface should be well controlled.