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Resistance Switching of HfO_2 Film and Its Application to Non-Volatile Memory

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1. Introduction

Recently, much attention has been paid to the resistance switching behaviors of various binary metal oxides such as TiO_2, NiO, and HfO_2 and their application to non-volatile memories [1-3]. The resistor component is composed of oxide sandwiched between two metal electrodes, which is the same metal-insulator-metal (MIM) structure as the capacitor in a charge-stored conventional DRAM device. However, a plausible origin of resistance switching and an optimized device structure with suitable materials has not yet been fully solved. In this work, the switching behaviors and device characteristics of resistors consisting of HfO_2 film and several metal electrodes are presented. As a result, we proposed a suitable oxide fabrication process and device structure with HfO_2 and top metal electrodes for the operation of resistance change RAM(ReRAM).

2. Experimental

The ReRAM devices with MIM structure were made as follows: Mo metal was deposited on a p-type Si wafer by rf magnetron sputter system at room temperature as a bottom electrode(BE). A HfO_2 film was deposited on the BE by atomic layer deposition (ALD) system (made by QUROS) at 300°C with $Hf(NCH_3C_2H_5)_4$ and H_2O. Additionally, O_3 and D_2O were also used to investigate the oxidant effect to resistance switching. Selected area of HfO_2 film was removed by reactive ion etcher to make BE bare. The top electrodes(TEs) of Mo, Ru, and Pt were then deposited by the rf magnetron sputter system and the final patterning was performed by conventional liftoff method. The material properties were identified by transmission electron microscopy (TEM), X-ray diffraction (XRD), and atomic force microscopy(AFM). And the resistance switching characteristics were evaluated by Agilent 4155A semiconductor parameter analyzer.

3. Results and Discussion

Fig. 1 is the cross-sectional TEM image of $Ru/HfO_2/Ru$ structure with 17 nm-thick HfO_2. And Fig. 2 shows the XRD peaks of $HfO_2/Ru/Si$ and Ru/Si. Both results indicate that HfO_2 film is amorphous due to its low temperature growth process. This as-grown HfO_2 film on metal electrode has a dielectric constant of 20, which is evaluated from the C-V curves of MIM structure. The amorphous HfO_2 film by ALD technique results in more significantly smooth surface morphology than that of Ru BE. Fig. 3 is the AFM image of HfO_2/Ru with RMS of 0.23 nm.

Fig. 4 shows the typical resistance switching characteristics of $Mo/HfO_2/Mo$ resistors, where the oxide is grown with the respective oxidant, H_2O, D_2O, and O_3, during ALD process. The devices fabricated with H_2O and D_2O well exhibit bistable low and high resistance states (LRS and HRS) whereas that of the O_3 oxidant shows only the current curves of broken insulator even in its lower current compliance. In case of D_2O oxidant, the lower current level at LRS and higher switching voltages (reset(Vr) and set(Vs) voltages) are shown. The sample with O_3 only shows a hard and sharp breakdown and higher breakdown voltage at fresh I-V curve compared to those with H_2O and D_2O as depicted in Fig. 5. O_3 in ALD process makes higher chemical binding and no contamination of hydroxyl ligand in oxide. It suggests that the resistance switching originates from the soft or incomplete breakdown of oxide.

The switching behaviors of the resistor with H_2O-processed HfO_2 were investigated. The variation of I-V curves for resistance switching is revealed in Fig. 6 with several TEs. The terms of switching voltages, voltage width(ΔV=Vs-Vr) between them, and resistance ratio significantly depends on TE. For example, the distributions of switching voltages for three electrodes, Mo, Ru, and Pt, with the same Mo BE are drawn in Fig. 7. These values are weakly dependent on the BEs, which means that the switching behaviors are greatly governed by the anodic electrode. In addition, the mean values of ΔV are 0.2, 2.2, and 4.8V for Mo, Ru, and Pt, respectively. The switching voltages and ΔV are assumed to be related to the effective work function of the TEs. The metal electrode with higher work function gives rise to a wider ΔV. Here, the wider ΔV with narrower distribution of both switching voltages can enhance the stability and reliability of device operation derived by the monopolar voltage sweep or pulse. However, the metal with higher work function has higher switching voltages in this study. Therefore, Ru as a TE is promising for positive voltage operation with the relevant Vr and Vs (< 5V) and relatively wider voltage gap between them.

Reliable and robust ReRAM device characteristics with Ru top electrode are also obtained from the retention and endurance tests. The results of retention test at 1.5V suggests long lifetime as shown in Fig. 8. Fig. 9 is the endurance result of sensing current at 0.5 V during cycles of switching. Each resistance ratio between LRS and HRS is larger than 10.

4. Conclusions

The resistance switching characteristics of amorphous, thin, and smooth HfO_2 film were investigated with the oxidant effect during ALD process. Ru is proposed as a TE due to its suitable switching voltages, wider voltage gap, and high reliability for ReRAM application.

Acknowledgements

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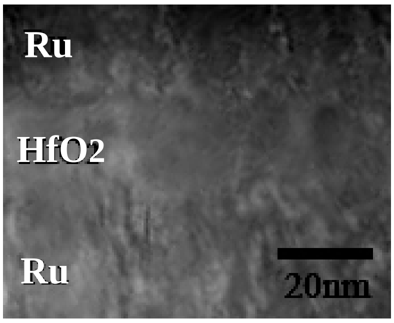

Fig. 1 Cross-sectional TEM image of Ru/HfO_2/Ru resistor with HfO_2.

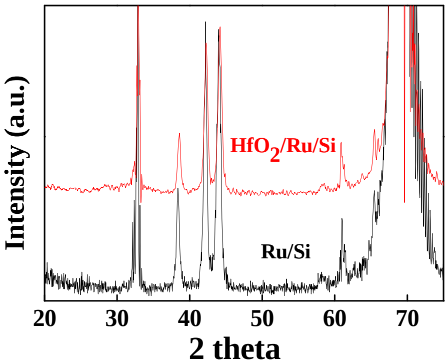

Fig. 2 XRD results of both HfO_2/Ru/Si and Ru/Si.

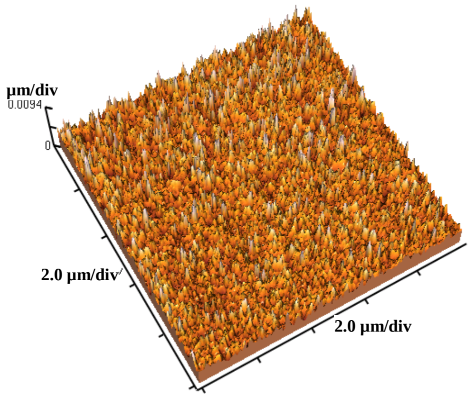

Fig. 3 AFM image of HfO_2/Ru/Si with RMS of 0.23nm.

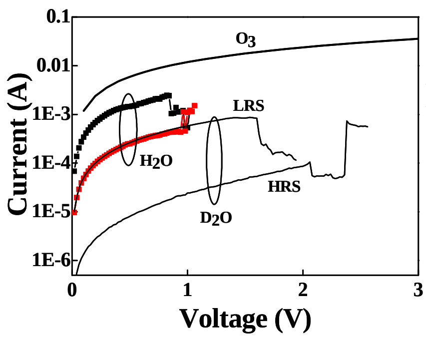

Fig. 4 Resistance switching behaviors of HfO_2 films deposited with H_2O, D_2O, and O_3, respectively.

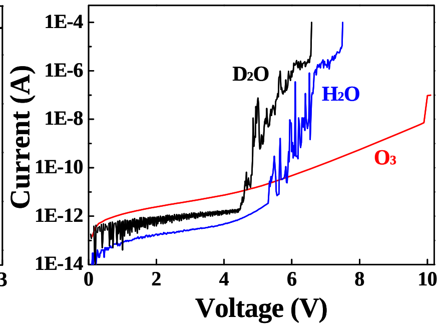

Fig. 5 Fresh I-V of HfO_2 films deposited with various oxidants with current compliance.

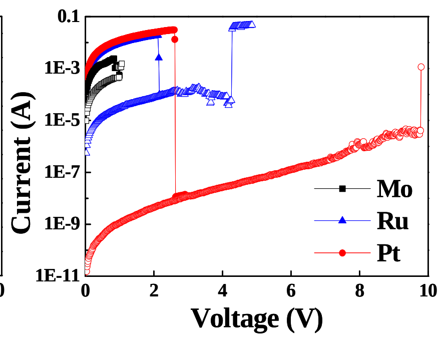

Fig. 6 Resistance switching behaviors of metal/HfO_2/Mo resistors (Metal= Mo, Ru, and Pt).

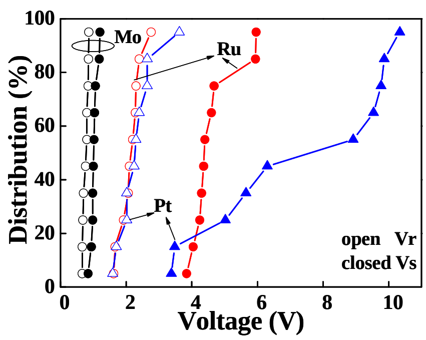

Fig. 7 Distribution of switching voltages of HfO_2 with Mo, Ru, and Pt top electrode, respectively.

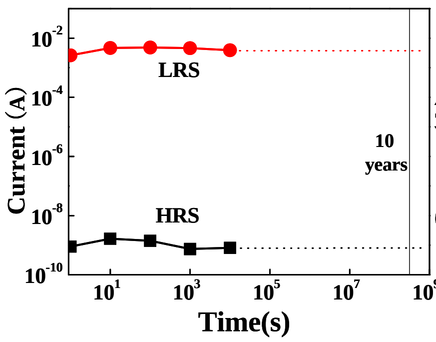

Fig. 8 Retention test of Ru/HfO_2/Mo resistor at 1.5V.

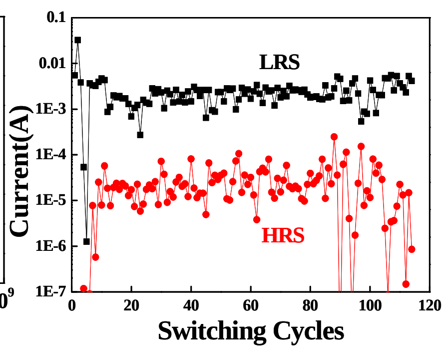

Fig. 9 Endurance of Ru/HfO_2/Mo resistor at 0.5V.