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Effects of Oxygen Precursor on Resistive Switching Properties of CMOS Compatible HfO$_2$-Based RRAM

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Abstract: In this work, we investigate the resistive switching behaviors of HfO$_2$-based resistive random-access memory (RRAM) in two different oxidants (H$_2$O and O$_3$) in an atomic layer deposition system. Firstly, the surface characteristics of the Ni/HfO$_2$/Si stack are conducted by atomic force microscopy (AFM). A similar thickness is confirmed by scanning electron microscope (SEM) imaging. The surface roughness of the HfO$_2$ film by O$_3$ (O$_3$ sample) is smoother than in the sample by H$_2$O (H$_2$O sample). Next, we conduct electrical characteristics by current–voltage (I–V) and capacitor–voltage (C–V) curves in an initial process. The forming voltage of the H$_2$O sample is smaller than that of the O$_3$ sample because the H$_2$O sample incorporates a lot of H$^+$ in the film. Additionally, the smaller capacitor value of the H$_2$O sample is obtained due to the higher interface trap in H$_2$O sample. Finally, we compare the resistive switching behaviors of both samples by DC sweep. The H$_2$O sample has more increased endurance, with a smaller on/off ratio than the O$_3$ sample. Both have good non-volatile properties, which is verified by the retention test.

Keywords: memristor; resistive switching; metal oxides; atomic layer deposition; HfO$_2$

1. Introduction

Resistive switching is a physical behavior where at least two conductance levels are reversible with non-volatile properties in the metal–insulator–metal structure [1–4]. The conductance change can be controllable by external bias. The emerging memory in which resistive switching is observed can be divided into three categories. RRAM includes a lot of materials, including metal oxide, metal nitride, silicon-based materials, and organic materials that exhibit various unipolar and bipolar resistive switching behaviors [2]. Phase-change random-access memory (PRAM) shows unipolar resistive switching in which the phase of Ge$_2$Sb$_2$Te$_5$ can be reversible by a heater such as TiN [5]. Magnetoresistive random-access memory (MRAM) also shows resistance change by controlling the magnetization of magnetic material [6]. RRAM has the advantage of being capable of tunable resistive switching, which is applicable to the various application as storage memory [7–20], logic-in-memory [21], and neuromorphic computing [22–40]. Moreover, RRAM shows low-power operation, high endurance, good retention, high-density integration, and good complementary metal–oxide–semiconductor (CMOS) compatibility in terms of process and material. Until now, metal-oxide-based RRAMs such as HfO$_2$ and TaO$_x$ show superior performance in terms of endurance, retention, the uniformity of switching parameters, and reproducibility over other material systems [41,42].

The resistive switching characteristics of RRAM depends on the materials of the top and bottom electrode and the insulator [1,2]. For example, metal oxides such as HfO$_2$ are used for RRAM. Diffusive electrodes such as Ag and Cu are the source of the conducting filament [18,43]. On the other hand, the oxygen vacancies can act as conducting filament when using non-diffusive electrodes such as Pt, Al, and TiN [44–46]. The deposition technique of the insulator plays an important role in the resistive switching properties. For example, the atomic layer deposition (ALD) and chemical vapor deposition (CVD)
techniques and a sputtering system are the most common ways for the insulator to act as a resistive switching layer. ALD is particularly suitable for the precise deposition of thin film (thinner than 5 nm) [47]. An ALD-deposited HfO$_2$ dielectric is commonly used as a gate oxide in the metal–oxide–semiconductor field-effect transistor (MOSFET) because HfO$_2$ has a higher dielectric constant than SiO$_2$ [48]. Moreover, ALD-deposited HfO$_2$ film is the leading material for RRAM application [49,50]. Until now, excellent resistive switching memory properties for variability, endurance, retention were reported in HfO$_2$-based RRAM [44,50]. ALD is suitable for 3D vertical RRAM structures due to its superior step coverage [51]. The electrical and material characteristics of ALD-deposited HfO$_2$ can be varied according to the metal and oxygen precursors. There are several previous works for ALD-HfO$_2$-based RRAM and HfO$_2$ film itself [52–56]. The effects of the process temperature and plasma parameters on the material properties of ALD HfO$_2$ film are discussed in [52]. Cell-to-cell variation was experimentally verified 1T1R (1 transistor + 1 resistor) based on HfO$_2$ RRAM devices [53]. The scavenging effect of Ti was discussed regarding a Co/HfO$_2$/Ti device [54]. The oxygen vacancies were considered for resistive switching in the Ti/HfO$_x$/Pt structure [55]. The resistive switching characteristics were modified by adding Al in a HfO$_2$ film [56].

In this work, two HfO$_2$-based RRAM samples were prepared with different oxygen precursors (H$_2$O and O$_3$). The surface analysis was conducted by AFM imaging, and the similar thickness of HfO$_2$ in two samples was confirmed by SEM imaging. Next, the electrical characteristics of the two samples were compared by initial C–V and I–V curves. Finally, we compared the basic properties, such as the endurance, retention, HRS, and LRS distribution, of RRAM in two samples.

2. Materials and Methods

Two HfO$_2$ RRAM devices with different oxygen reactants were fabricated as follows. Organic material of a 6-inch silicon wafer was removed by SPM and HPM standard cleaning processes. Ion implantation was carried out by a medium current ion implanter (Varian, E220) to increase the conductivity of silicon substrates and use them as bottom electrodes. The dose of BF$_2^+$ was $5 \times 10^{15}$ cm$^{-2}$, and the acceleration energy was 40 KeV for the p$^{++}$-Si surface. Here, we removed native oxide by HF dipping and metallic contaminants by HPM cleaning. After the bottom electrode was fabricated, a 20 × 20 mm specimen sample was produced using a dicing saw. Additionally, HfO$_2$ 7 nm as the switching layer was deposited using ALD by tetrakis (dimethylamino)hafnium (TDMAHf) and other oxygen reactants (O$_3$ and H$_2$O). First, the ALD (CN1, Atomic premium) process sequence of O$_3$-based HfO$_2$ for one cycle is as follows. TDMAHf 0.5 s/N$_2$ purge 6 s/O$_3$ 0.5 s/N$_2$ purge 9 s, shown in Figure 1a. Second, the ALD process sequence of H$_2$O-based HfO$_2$ for one cycle is only different from the last oxygen reactants’ purge time at 20 s, shown in Figure 1b. In this work, we optimized the growth per cycle in HfO$_2$ with the H$_2$O precursor by controlling the reactant dosing time, reactant purge time, and stage temperature, shown in Figure S1. Because H$_2$O is not easily removed from the chamber, it requires a relatively long purge time compared to O$_3$. In order to deposit the same target thickness of 7 nm, O$_3$ and H$_2$O were used to perform 68 cycles at 350 °C and 84 cycles at 260 °C, respectively. Finally, a 100 nm thick Ni as the top electrode was deposited as TE by an E-gun evaporator (MAESTEK, ZZS550, Pyeongtaek, Korea), and the cells were separated using a shadow mask. A Keithley 4200-SCS semiconductor parameter analyzer and a 4225-PMU Solon. OH, USA in the probe station were used to measure the electrical characteristics. Additionally, a bias was applied to the top electrode and the bottom electrode was grounded.
3. Results and Discussion

We confirmed the thickness of the dielectrics by cross-sectional SEM imaging before we compared the resistive switching properties of both samples, shown in Figure 2a,b. The HfO$_2$ layer of the H$_2$O sample and O$_3$ sample were both about 7 nm, which corresponded to the target deposition thickness. The resistive switching could be affected by the roughness effects [57]. Figure 3a,b shows the surface of two samples of HfO$_2$ measured in the non-contact mode of AFM. Each mean value of roughness was 0.245 nm and 0.262 nm for the O$_3$ sample and H$_2$O sample, respectively. It was found that the surface roughness of the O$_3$ sample and H$_2$O sample did not differ greatly.

Next, we investigated the initial state to find the effect of oxygen precursor on the electrical characteristics of the HfO$_2$-based metal–oxide–semiconductor capacitor. Figure 4a,b show the C–V characteristics with different frequency ranges (1 kHz to 500 kHz). The O$_3$ sample has higher capacitance values than the H$_2$O sample. Although the O$_3$ precursor has a stronger oxidizing ability than H$_2$O precursor, unwanted interfacial growth of SiO$_x$ on a silicon substrate is higher [58,59], but since there are fewer interface traps at the interface in the O$_3$ sample, it was judged that the capacitance value will be larger in O$_3$ sample. A correlation study of the growth rate, thickness uniformity, stoichiometry, and hydrogen impurity level was discussed in previous work [60].

Figure 1. ALD (atomic layer deposition) process for HfO$_2$ dielectric. (a) O$_3$ precursor and (b) H$_2$O precursor.

Figure 2. Cross-sectional SEM (scanning electron microscope) images of (a) O$_3$ sample and (b) H$_2$O sample of Ni/HfO$_2$/Si RRAM (resistive random-access memory) devices.
Next, we focus on the resistive switching behavior in both samples. Figure 6a shows the typical I–V characteristics of set and reset processes in bipolar resistive switching. It is noted that the forming and set processes at negative bias are conducted to exclude the Ni diffusion and consider the resistive switching by oxygen vacancies. The set process is conducted with a compliance current (CC) of 1 mA that can confine the conducting filament properly in the HfO₂ dielectrics. As the current increases rapidly at the set voltage, 

Figure 3. AFM (atomic force microscopy) images of (a) O₃ sample and (b) H₂O sample of Ni/HfO₂/Si RRAM devices.

Figure 4. (a) Typical I–V forming curves and (b) forming voltage distribution of O₃ and H₂O samples. CC: compliance current.

Figure 5a shows the I–V characteristics in both samples. The O₃ sample requires approximately 2 V higher forming voltage than the H₂O sample. Forming voltage is an initial characterization of the device and cannot be controlled, unlike the set voltage and reset voltage. Forming voltage distribution in 20 cells is displayed in Figure 5b. In terms of initial current, the H₂O sample has a higher initial current than the O₂ sample. For the H₂O sample, the quality of the thin film is not good, and there are a lot of (C, H) impurities in the dielectric [57,58]. However, since there are relatively many oxygen defects, which could be beneficial to RRAM behaviors, it is easier to operate the resistive switching with a smaller voltage compared to O₃ RRAM. In general, if there are many defects of the dielectric and interface in MOSFET, the performance of the transistor deteriorates, but in the case of RRAM, an oxygen defect should exist for the current to flow well. In addition, C, H impurity can become a conductive path, which additionally provides a path for electrons to move, and the operating voltage is lowered [61].
the state of the RRAM devices is switched from the high-resistance state (HRS) to the low-
resistance state (LRS) by the set process. The conducting filament is formed by an increase
in oxygen vacancies when the electric field is applied to the RRAM devices. On the other
hand, the reset process occurs with a positive bias. The conducting filament composed of
oxygen vacancies is ruptured with an opposite bias of the set process. Figure 6b,c show
the endurance cycles of O3 and H2O samples, respectively. The LRS resistance is similar
due to the same controlled CC of 1 mA in both samples. However, the HRS of the H2O
sample has a larger variation during cycling than the O3 sample. This is attributed to the
fact that the deep reset of the O3 sample could be irregular. These properties are confirmed
to be the cumulative probability of HRS and LRS distribution again in Figure 6d. Finally,
a retention test was conducted in the LRS and HRS to check the non-volatile property of
both samples. All have no significant degradation for the 10,000 s in Figure 6e.

![Figure 5](image.png)

Figure 5. C–V curves of (a) O3 sample and (b) H2O sample of Ni/HfO2/Si RRAM devices.

![Figure 6](image.png)

Figure 6. (a) I–V curves of two Ni/HfO2/Si RRAM samples. Endurance cycles of (b) O3 sample and (c) H2O sample. (d) Cumulative probability two samples in LRS (low-resistance state) and HRS (high-resistance state). (e) Retention test for two samples.
4. Conclusions

In summary, the memristive switching behaviors of HfO$_2$-based RRAM is studied in two different oxidant precursors (H$_2$O and O$_3$) in the ALD technique. Firstly, the surface characterization of the Ni/HfO$_2$/Si RRAM device is performed by AFM. The surface roughness of the O$_3$ sample is better than in the H$_2$O sample. Next, the electrical characteristics of the initial state and forming process are performed by I–V and C–V curves. The forming voltage of the H$_2$O sample is smaller than that of the O$_3$ sample because the H$_2$O sample includes more hydrogen ions in the HfO$_2$ dielectric. Additionally, the smaller capacitance of the H$_2$O sample is measured due to a lot of interface traps in the H$_2$O sample. Finally, the resistive switching behaviors of both samples are evaluated by the DC sweep mode. The H$_2$O sample has a higher endurance and smaller on/off ratio than the O$_3$ sample. Good non-volatile properties in the LRS and HRS are observed, which is confirmed by the retention test.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/met11091350/s1. Figure S1: HfO$_2$ ALD (atomic layer deposition) optimization with H$_2$O as oxygen precursor. (a–d) Growth per cycle (GPC) as a Figure 2. Thickness as a function of ALD cycles.

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