Reversible nonvolatile and threshold switching characteristics in Cu/high-k/Si devices

Chandreswar Mahata¹, Wonwoo Kim², Shiwhan Kim², Muhammad Ismaïl², Min-Hwi Kim¹, Sungjun Kim²,¹, and Byung-Gook Park²b)

Abstract Here, the resistive switching properties of Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si devices are investigated in details. Both memory switching and threshold switching behaviors observed under different current compliance conditions. The transition between two switching modes is possible. Cu ion diffusion form conductive filaments inside the insulator and formation/dissociation mechanism induced the switching phenomenon. The device performances under both memory switching and threshold switching are possible for non-volatile storage memory and selector applications, respectively.

Keywords: resistive switching, atomic layer deposition, CBRAM, copper, high-k dielectric

Classification: Electron devices, circuits and modules

1. Introduction

Recently, resistive random access memory (RRAM) attracts much attention for next generation nonvolatile memory because of its simple stacked structure, high-speed operation, long-time retention, excellent cycling endurance, high-density integration, and complementary metal-oxide-semiconductor (CMOS) compatibility [1, 2, 3, 4]. The simple structure of RRAM consists of sandwiched insulating layer between top and bottom electrode. RRAM exhibits successive transition from high resistance state (HRS) to low resistance state (LRS) under the current compliance. Different transition metal oxide materials such as Al₂O₃, Ta₂O₅, ZrO₂, TiO₂, NiO, Nb₂O₅, and HfO₂ are broadly used due to its simple deposition process and compatibility with CMOS process [5, 6, 7, 8, 9, 10]. Among them hafnium oxide (HfO₂) is promising material for resistive switching material due to high dielectric constant and bandgap and compatible with Si [11]. On the other hand, Al₂O₃ is one of the widespread high-k dielectric to replace SiO₂ due to its good thermal stability, high crystallization temperature, wide band gap and low processing temperature, and have attracted more attention in the field of RRAM [12, 13].

Resistive switching effect in general is originated by forming, dissolution, and recovery of conductive filaments in RRAM devices. In most of the cases, the filament formation occurs from oxygen vacancy generated from redox present in the insulator typically referred to as valence change metallization (VCM) cells. On the other hand, the switching phenomenon is controlled by metal filaments (MF) from electrochemically active electrodes such as Cu and Ag, which is known as electrochemical metallization cells (ECM). In both cases RRAM devices demonstrates good cycling endurance, low switching time and current [14, 15, 16, 17]. ECM memory cell based on metallic ion migration inducing resistive switching with various insulating materials has attracted attention. The whole mechanism involves multiple steps. At first anodic dissolution of metal occurs due to the applied electric field on the anode side, consequently the metallic (Cu, or Ag) ions are drifted towards insulator film. Finally, the ions are electro-crystallized, form the filament in between anode and cathode, and makes the switching cell in LRS (ON).

Under the opposite polarity electric field, the electrochemical dissolution of conductive filament (CF) happens at the weakest point and the cell comeback to HRS (OFF). Therefore, the resistance of RRAM device can be switched between HRS and LRS under electrical stimuli by formation/dissolution of nanoscale conductive filaments (CFs) inside RS layer. However, ion injection from whole anode leads to poor uniformity of RS and inferior retention of different resistance state, which affects the device reliability [18, 19, 20]. Multiple CFs and cathode surface roughness can also play a role for poor RS uniformity and accumulated active metal species at cathode surface can deteriorate the device reliability [21, 22]. Highly doped Si electrode is a good candidate among the various bottom electrode (cathode) due to its compatibility in CMOS. The insulating switching layer can be deposited directly on doped Si, which reduces processing steps. Recent studies demonstrated that uniform and stable RS properties can be achieved with different metal oxides on doped Si bottom electrode (BE) [23, 24, 25, 26, 27].

In this work, resistive switching properties of Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si have been investigated.

2. Experiments

The fabrication of Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si devices as follow: Ion implantation was used to form heavily

¹Inter-university Semiconductor Research Center (ISRC) and the Department of Electrical and Computer Engineering, Seoul National University, Seoul 08826, South Korea
²School of Electronics Engineering, Chungbuk National University, Cheongju 28644, South Korea

a) sungjun@chungbuk.ac.kr
b) bgpark@snu.ac.kr

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doped Si bottom electrodes. BF$_2^+$ ions were implanted into the silicon surface at a dose of $5 \times 10^{15}$ cm$^{-2}$ and an energy of 40 keV, and the annealing was performed for activation. The measured sheet resistance of doped silicon bottom electrode was 30.4$\Omega$/sq. Al$_2$O$_3$ and HfO$_2$ dielectrics were deposited using atomic layer deposition (ALD). TMA and O$_3$ were used as precursors of Al$_2$O$_3$, and TEMAHf and O$_3$ were used of HfO$_2$ films. Cu was deposited as a top electrode by a thermal evaporator.

All electrical properties were characterized using a DC voltage sweep with a Keysight B1500A semiconductor parameter analyzer (SPA). For the device operations, the Si bottom electrode was grounded and the Cu electrode was controlled.

3. Results and discussions

To investigate the resistive switching behavior of the Cu/Al$_2$O$_3$/p-Si and Cu/HfO$_2$/p-Si devices, all DC I-V characteristics were measured at room temperature. Fig. 1 shows the both bipolar resistive switching of Cu/Al$_2$O$_3$/p-Si and Cu/HfO$_2$/p-Si under the current compliance (CC) of 1 mA and threshold switching under CC of 1 $\mu$A for different thickness of insulating layer (3.5 nm and 6 nm). When the CC was set to 1 mA, with the increase of positive voltage the devices switches from HRS to LRS (SET) abruptly and upon sweeping under negative bias voltage the devices switch back to HRS (RESET) which indicates typical non-volatile bipolar memory switching behavior.

However, when the CC is 1 $\mu$A, threshold switching is observed upon sweeping from 0 to 8 V and the current level abruptly increases and reaches to on state and this voltage is defined as $V_{th}$. After sweeping from 8 V to 0 current level gradually decreases and the devices switched back to HRS and this voltage is defined as $V_{hold}$. It is noted that transition of bipolar switching and threshold switching is available in both directions. This device has the advantage that it can return to its original state when the state hazard occurs and maintain the original switching.

The Cu/high-$k$/p-Si schematic device structure is shown in Fig. 2 with Si BE, RS layer, and Cu top electrode. The mechanism for CF formation described in several previously reported articles [28, 29, 30, 31]. Under the external bias, Cu ions migrate through the defects sites of the insulating high-$k$ RS layer. Diffused Cu ions electrochemically reacts to the HfO$_2$ and Al$_2$O$_3$ and forms the conical type metallic filament as shown in Fig. 2. It is noted that for HfO$_2$ the SET voltage is lower than the Al$_2$O$_3$ for the thickness of 3.5 nm that could be possible due to the rapid migration of Cu in HfO$_2$ due to higher grain boundary defects or higher charge trapping density [29, 30]. Under the RESET operation with a negative bias, Cu ions partially return to the Cu top electrode, which is a cause for annihilation of conductive filament paths as shown by the schematic of SET and RESET process in Fig. 2. In addition, it is important to notice that this columnar Cu CF contribute at the initial in both devices and no forming operation was needed to trigger the device, which is promising for this device application. In case of lower CC at 1 $\mu$A the threshold switching is related to the formation and self-dissolution of weak Cu CFs. This phenomenon also attributed to the minimal residual of Cu at bottom high-k/Si interface, which is an advantage of Si bottom electrode [32].

![Fig. 1. Transition of bipolar memory switching to threshold switching in I-V characteristics with semi-log scale for Cu/Al$_2$O$_3$/p-Si with (a) 3.5 nm Al$_2$O$_3$ and (b) 6 nm Al$_2$O$_3$ under a CC of 1 mA and 1 $\mu$A. Bipolar to threshold switching transition of Cu/HfO$_2$/p-Si with (a) 3.5 nm HfO$_2$ and (b) 6 nm HfO$_2$ under a CC of 1 mA and 1 $\mu$A.](image)

![Fig. 2. The basic schematic structure of RRAM using top electrode (TE) as Cu and Si as bottom electrode (BE) with Al$_2$O$_3$/HfO$_2$ as dielectric material along with the operating set/reset in RRAM device.](image)
Al₂O₃ due to its polycrystalline nature with more grain boundary defects which leads to easier migration of Cu ions. Different previous reports already have confirmed that crystallization is favorable in case of HfO₂ compared to Al₂O₃ for direct deposition on Si [33, 34, 35, 36].

Fig. 4 displays the endurance characteristics of the memory switching for 50 switching cycles for Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si with different thickness of high-k under CC of 1 mA. Although the resistance of LRS and HRS shows slight variations, the effective switching memory window for Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si is significant and the values are of the order of 10⁵ measured at 0.2 V for different thickness of Al₂O₃ and HfO₂.

Fig. 5 shows the retention behavior of both Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si devices. LRS and HRS maintains without severe degradation for up to 10⁷ s read at 0.2 V at 85°C. This measurement was done at Icc of 1 mA to demonstrate the stability or non-destructive nature of the filament at LRS. The resistances of the device at HRS and LRS are almost uniform, as shown in Fig. 5 confirming the nonvolatile characteristics of the device.

4. Conclusion

We characterized non-volatile switching and threshold switching of Cu/Al₂O₃/p-Si and Cu/HfO₂/p-Si devices. Reversible switching for two switching modes are achieved. The switching models of two devices have been discussed through Cu diffusion and statistical switching parameters for devices of different thickness are investigated. Endurance cycle testing and retention characteristics for non-volatile memory are verified.

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