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Ultra-large resistance ratio of silver programmable metallization cell with stacked silicon oxide films

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ABSTRACT

Characteristics of silver programmable metallization cells (Ag-PMCs) with single and stacked silicon oxide (SiO_x) films were investigated. The oxygen to silicon intensity ratio of chemically-deposited SiO_x and thermally-grown SiO_2 films was analyzed by the energy dispersive X-ray spectroscopy (EDS). Though the set and reset voltages of Ag-PMCs with stacked SiO_x films were increased owing to the high stoichiometry of thermally-grown SiO_2 layer, the resistance ratio of more than 10^6 can be realized by the thick Ag conductive filament (CF) for the low resistance value at low resistance state (LRS). The thermally-grown SiO_2 film can also prevent the regeneration of Ag-CF during retention test, leading to the superior retention properties for more than 10^4 s. The Ag-PMCs with stacked SiO_x films can sustain a resistance ratio of five orders of magnitude for more than 400 times stable set and reset cycling, suitable for future multi-bit/cell nonvolatile memory operation.

1. Introduction

Conventional floating gate flash memory has encountered some issues when the device scales; for instance, the low program/erase speeds and poor data retention have proven hard to be solved [1–3]. Thus, many devices have been investigated as promising approaches [4–7], from which the resistive random access memory (RRAM) is considered as the most attractive one because of the advantages of simple structure, easy fabrication, fast operation speed, excellent scalability, multi-level potential, and compatible with complementary-metal-oxide-semiconductor (CMOS) process [4]. RRAM can recyclingly change the conductivity of the resistive switching layer between the high resistance state (HRS) and low resistance state (LRS) under the sweep or pulse voltage operation. The simple metal-insulator-metal (MIM) structure with a dielectric material, such as SiO_2, NiO, TiO_2, HfO_2, and Gd_xO_y, has been shown to exhibit excellent bistable resistive switching behavior [8–12]. Furthermore, there are lots of resistive switching mechanisms proposed for the RRAM devices. For example, the conductive filament (CF) in insulator, such as the metal ions, has been proposed and also named as the programmable metallization cell (PMC) or the conductive bridge RAM (CBRAM) [13]. The PMC utilizes the electrochemical formation and rupture of metallic pathways in thin films of solid electrode to get low and high resistance respectively. The use of silver (Ag), copper (Cu) and nickel (Ni) as the electrochemically active electrode has been widely suggested to realize the resistive switching [14–16]. Compared with the conventional RRAMs, PMC possesses lower operation voltage of several hundred mV, lower programming current with the order of 10–100 μA, higher switching speed of less than 50 ns, and the feasibility of multi-bit storage because of the linear relationship between on-state resistance and writing current [17].

It is reported that a high on/off-state resistance ratio plays an important role in the applications of RRAM because it directly influences the accuracy of set and reset operations [18]. Generally speaking, a resistance ratio of larger than 10 is required to distinguish two resistance states in circuit design [19]. In some RRAMs, especially for the devices with CF of oxygen vacancies, the resistance ratio can be as high as five to six orders of magnitude with stable retention and sufficient endurance properties [20]. Such a huge resistance ratio can be ascribed to the large resistance at high resistance state ($>10^8$ Ω) by completely cutting off the filament with a tunnel barrier of a quite small MIM devices (<10 μm^2) [20,21], providing the possibility of realizing a high-density nonvolatile memory by means of the multi-bit storage [11]. Nevertheless, for the conventional PMCs, the resistance ratio is

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presented to be lower than 10^4 [14–16], which limits the use for multi-level cell operation. In this work, an ultra-large on/off-state resistance ratio of the silver programmable metallization cells (Ag-PMCs) with stacked silicon oxide (SiO_x) films was proposed. The chemically-deposited SiO_x and thermally-grown SiO_2 films were stacked as the active layer (solid electrolyte). With the introduction of high stoichiometric thermally-grown SiO_2 film, the resistance ratio of more than six orders of the Ag-PMCs can be achieved, owing to the reduction of resistance at LRS. The conductive mechanism of the devices were proposed and found that the low resistance at LRS can be ascribed to the thick Ag-CF by the large operation voltages. The retention and endurance characteristics are significantly enhanced to more than 10^4 s and 400 times respectively for the Ag-PMCs with the stacked SiO_x films.

2. Experimental

Al/Ag/SiO_x/n^+-Si devices were fabricated on 4-inch heavily-doped n-type (100) Si wafers. All samples were first cleaned by a standard Radio Corporation of America (RCA) cleaning method. Some samples were subjected to the horizontal furnace in O_2 ambient at 850 °C to thermally grow a 15-nm-thick SiO_2 film. Besides, some samples were subjected to the plasma-enhanced chemical-vapor-deposition (PECVD) system in SiH_4 and N_2O ambient of the flow rate of 5 and 200 sccm respectively at 300 °C by a radio frequency power of 100 W at 0.8 mbar to chemically deposit a 15-nm-thick SiO_x film. The chamber of PECVD system was first pumped down to 4×10^{-5} mbar before fabrication and the purity of SiH_4 and N_2O ambient was both 99.999%. Subsequently, another 15-nm-thick SiO_x layer was deposited by the PECVD system to obtain a totally 30-nm-thick SiO_x layer, and denoted as P/D and P/P respectively. For comparison, some samples were thermally-grown and PECVD-deposited a 30-nm-thick SiO_x layer and denoted as D and P respectively. Then, a 50-nm-thick silver (Ag) film was deposited by a thermal evaporator at 1.33×10^{-6} mbar with a pure Ag bullet (99.99%) as the top electrode (TE). To avoid the probing issue of such a thin Ag film, a 300-nm-thick aluminum (Al) film was also deposited by a thermal evaporator at 1.33×10^{-6} mbar with a pure Al bullet (99.999%) on the Ag TE as metal contact. Meanwhile, an area of 200 μm in diameter was defined by the lift-off process. The schematic structures of the four-types of PMCs were illustrated in Fig. 1. The electrical properties of each PMC for at least 20 samples were measured by using the Agilent B1500A semiconductor device parameter analyzer. The voltage was applied on the silver TE and the n^+-Si bottom electrode (BE) was connected to the ground. The current compliance (CC) of 500 μA was used at set process to control the size of conductive filament. In addition, the high-resolution transmission electron microscopy (HRTEM) image of the sample P/D was investigated in Fig. 2(a). A stacked SiO_x film of about 30 nm was noted. In Fig. 2(b), the energy dispersive X-ray spectroscopy (EDS) spectra were also analyzed to obtain the oxygen to silicon intensity ratio. A distinct ratio difference between the thermally-grown and PECVD-deposited SiO_x film was observed. The average oxygen to silicon ratio of top and bottom SiO_x film was approximately 1.68 and 1.96 respectively, indicating that the thermally-grown SiO_2 film was much more stoichiometric.

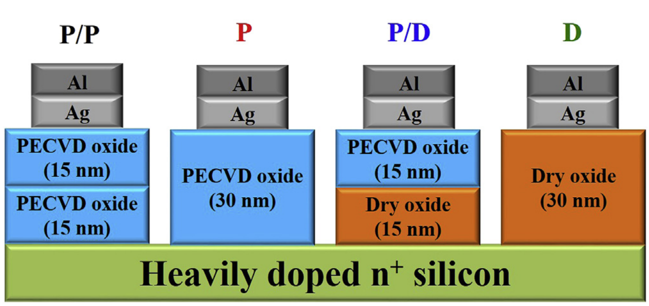

Fig. 1. Schematic structures of Al/Ag/SiO_x/n^+-Si PMCs with single and stacked SiO_x films. The sample with single thermally-grown SiO_2 film, single PECVD-deposited SiO_x film, stacked PECVD-deposited SiO_x films, and stacked PECVD-deposited SiO_x and thermally-grown SiO_2 films were denoted as D, P, P/P, and P/D, respectively. A totally SiO_x film thickness of 30 nm was obtained.

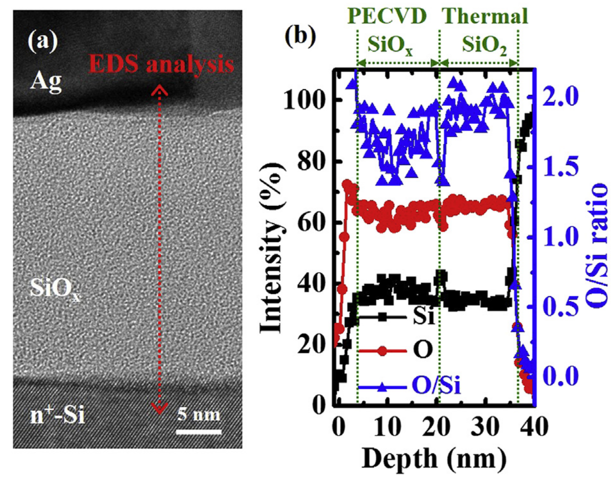

Fig. 2. (a) HRTEM image of the sample P/D. (b) EDS spectra of the sample P/D analyzed from the red line in HRTEM image of (a). The average oxygen to silicon ratio of top and bottom SiO_x film was approximately 1.68 and 1.96 respectively.

3. Results and discussion

Fig. 3 shows the typical current–voltage (*I*–*V*) characteristics of silver programmable metallization cells (Ag-PMCs) with single and stacked silicon oxide active layers. To operate the Ag-PMCs, a forming process is needed to form the silver conductive pathways. All samples present the bipolar resistive switching behavior with the set and reset operation at positive and negative TE bias respectively, except for the Ag-PMC with single SiO_2 layer fabricated by dry oxidation (sample D). When a negative TE bias is applied, sample D shows a dielectric breakdown instead of the

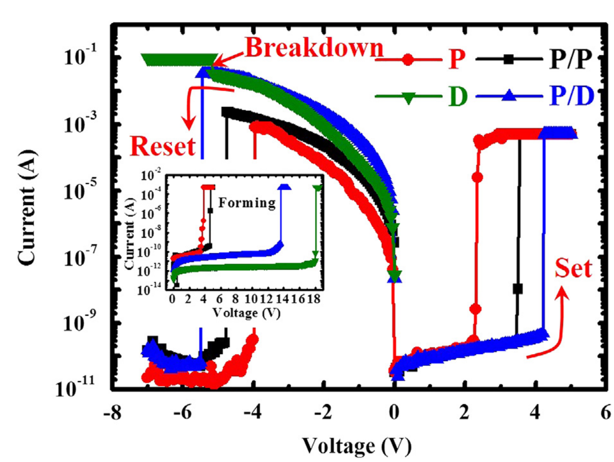

Fig. 3. Typical current versus voltage (*I*–*V*) characteristics of the Ag-PMCs with single and stacked SiO_x films. All samples presented the bipolar resistive switching behavior except of the sample D. The forming process was shown in the inset figure.