**Performance Variation of Solution-processed Memristor Induced By Different Top Electrode**

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Abstract

Al/TE (top electrode)/AlOx/Pt RRAM (resistive random access memory) devices with solution-processed spin-coated AlOx layers annealed at various temperatures (225/250/275°C) exhibited typical bipolar resistive switching performance with low SET/RESET voltage (< 4 V), larger ON/OFF ratio (> 103) and excellent stability (retention time over 104 s and endurance cycles more than 100). Ni and TiN were chosen as the TE, respectively. Better RS characteristics were obtained on Ni/AlOx/Pt RRAM devices with lower operating voltage and better stability. In addition, the voltage variation between Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices was investigated. Compared with Ni/AlOx/Pt RRAM devices, TiN/AlOx/Pt devices operated with higher operation voltage at various annealing temperatures, which indicated the influence of work function difference (△ΦM) between TE and BE (bottom electrode). The greater the △ΦM, the more energy consumption and the higher operation voltage were demanded.

**Keywords**: solution-processed, work function difference, RRAM

**Introduction**

It has been increasingly difficult for traditional silicon-based devices to meet the daily-increasing requirements of the development in the field of artificial neural networks (ANN). The future target of ANN systems is to emulated behaviors like the human brain such as including real-time decision making, sufficient risk assessment and emotional thinking [1-3]. Therefore, it is necessary to investigate devices with faster operation speed, better stability and higher economic efficiency. Resistive random access memory (RRAM) device has received extensive interest due to its outstanding resistive switching (RS) performance with single-digit-level operation voltage, pico-joule-level energy consumption, nanosecond-level operating rate and year-level service life [4-8]. The classic sandwich structure with metal-insulator-metal (MIM) of the RRAM device indicates the simplicity of structural configuration [4-6]. For now, some conventional materials have been chosen as candidates for the insulator layer because they have been confirmed with stable RS performance, including metal oxides (AlOx, NiO, HfOx) and solid electrolytes (Ag2Se) [9-16]. Besides, some other emerging materials are also under investigation such as biological materials (silk protein and albumen), polymer materials (polydiacetylene and polyvinyl alcohol), and two-dimensional materials (graphene oxide and molybdenum disulfide) [17-21]. Except for materials of the switching layer, materials of the electrode are also under discussion, which has a relationship with the switching mechanism of RRAM devices [4, 19-21]. For devices with active metal top electrodes (TEs) like Ag and Cu, it has been considered that metallic conductive filaments (CFs) comprising metal atoms determined the RS performance [20-25]. However, for RRAM devices with inert TE like Ni, TiN, Pt and Al, CFs based on oxygen vacancies in dielectric layers played dominating roles during the RS process [17-19]. In addition, the fabrication methods of insulator layers cannot be neglected, some RS thin films can be obtained by traditional methods like sputtering and atomic layer deposition (ALD) with stable performance while improved characteristics of insulator layers with higher cost-effectiveness can be presented with emerging fabrication methods such as solution-processed methods with spin-coating and drop-casting operations [8, 17-21].

In this work, in order to prevent the variation of the RS mechanism, Ni and TiN were chosen as TEs for RRAM devices with solution-processed spin-coated AlOx layers, respectively. The AlOx layers were fabricated at different annealing temperatures from 225°C to 275°C, with 50°C increments. Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices both presented the bipolar RS performance. Compared with TiN/AlOx/Pt RRAM devices, Ni/AlOx/Pt RRAM devices annealed at each temperature showed better characteristics with lower operating voltage and better stability. The variation of RRAM devices with Ni and TiN TE might be related to the work function difference (△ΦM) between the top and bottom electrode, which indicated that the greater the △ΦM, the more energy consumption and the higher operation voltage were demanded.

**Experimental**

**Preparation of precursor solution----**The solution-processed AlOx switching layer was fabricated from its precursor solution, which was synthesized by ~15 mL deionized (DI) water and ~ 14.0304 g aluminum nitrate nonahydrate (Al(NO3)3·9H2O). The 2.5 M precursor solution was continuously stirred in a beaker at room temperature until it was clear and transparent.

**Device fabrication----**As illustrated in **Figure. 1a**, the fabricated RRAM device with the structure of Al/TE/AlOx/Pt can be presented and materials of TE are Ni and TiN, respectively. Take the Al/TiN/AlOx/Pt RRAM device as an example. At first, to remove the organic and inorganic impurities, the purchased substrate comprising Pt/Ti/SiO2/Si was ultrasonically cleaned in acetone, ethanol, and DI water in sequence. The time for each ultrasonic cleaning process was 20 min. Then the 15-minute hydrophilic treatment in a vacuum with an expanded plasma cleaner (PDC-002 HARRICK PLASMA) was conducted to the cleaned Pt substrate, which enhanced the hydrophilia of the bottom electrode (BE) and made the entire spin-coating process easier to obtain. After the process of hydrophilic treatment, the prepared 2.5 M AlOx precursor solution was spin-coated in the air onto the Pt substrate with a spin rate at 3500 rpm and the spin time was 40 s. Then the device with the structure of AlOx precursor solution/Pt was annealed at the desired temperature (225/250/275°C) for 60 min in the air and a ~ 35 nm AlOx switching layer was grown successfully. Finally, a ~ 40 nm TiN layer and a ~ 20 nm Al layer were deposited onto the AlOx layer by thermal evaporator respectively. The TiN was chosen as the TE layer while the capper layer Al was used to prevent the external oxidation. The TE layer was deposited onto the switching layer through a shadow mask and a single TE was deposited with the size of 0.1 mm diameter determined by the mask aperture. **Figure. 1b** demonstrated the SEM image of the Ni/AlOx/Pt RRAM device.



**Figure 1.** (a) Schematic view of the RRAM device with the structure of Al/TE/AlOx/Pt. (b) An SEM image of Al/Ni/AlOx/Pt RRAM device.

**Results and discussions**

All electrical performance was characterized by an Agilent B1500A high-precision semiconductor analyzer (Agilent Santa Rosa, CA, USA). **Figure. 2** showed bipolar RS characteristics of both Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices with AlOx RS layers annealed at 225°C, 250°C and 275°C. All current-voltage (IV) curves presented the resistance change with the effect of SET and RESET operations. The SET and RESET processes were labeled with black and green color, respectively. We took **Figure. 2b** as an example. When the positive voltage was applied onto the TE layer during the SET process, the device switched from initial high-resistance-state (HRS) to low-resistance-state (LRS) with the abrupt increase of current, which was demonstrated by black arrow indications with black numbers in circles from ① to ④. The device was at ON state when the current increased up to the 1 mA compliance current (CC). Reversely, during the RESET process, the device transferred back to HRS with the effect of the negative electric field and finally reached the OFF state. The process was shown by green arrow indications with green numbers in circles from ⑤ to ⑧. The purpose of only CC-setting in the SET process was to prevent the device from being destroyed by a large current. To make the device switch back to HRS to the greatest extent, there was no CC-setting during the RESET process. According to our previous study [4, 8, 11], the solution-processed AlOx thin film could demonstrate RS behavior with the annealing temperature range of 200-300°C. Therefore, the desired annealing temperature for Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices in this work was 225°C, 250°C and 275°C. For all samples, Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices with AlOx layers annealed at 225°C demonstrated the highest operation voltages while the lowest operation voltages could be obtained at 250°C annealed devices. The best RS performance of Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices were both presented by their 250°C annealed samples, which might be associated with oxygen vacancy concentration of solution-processed AlOx layers [11]. For Ni/AlOx/Pt RRAM devices, compared with 225°C- and 275°C-annealed samples, samples with the AlOx layer annealed 250°C showed the lowest operation voltage (especially the ~1 V SET voltage), the most stable ON/OFF ratio (>100) and the slightest fluctuation of resistance values in endurance and retention properties. The same characteristics were observed on TiN/AlOx/Pt RRAM devices, samples with the AlOx layer annealed 250°C also demonstrated the lowest SET/RESET voltage around 1.2 V, the most stable ON/OFF ratio (>100) and the slightest fluctuation of resistance values in endurance and retention properties. Obviously, Ni/AlOx/Pt devices presented the lower operation voltage among RRAM devices annealed at all desired temperatures, which indicated that the material difference of TE had a significant influence on the RS behavior of the RRAM device [4, 17-20]. **Figure. 3** showed the results of voltage distribution for Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices annealed at 225/250/275°C during SET and RESET operations. The results also indicated the similar performance of IV curves that Ni/AlOx/Pt samples operated the excellent RS performance with lower voltage and lower energy consumption [4, 17-21].



**Figure 2.** Bipolar switching performance of Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices annealed at 225/250/275°C.



**Figure 3**. Statistic results of operation (SET/RESET) voltages distribution for Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices annealed at 225/250/275°C.

The endurance and retention performance of Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices with their solution-processed AlOx layers annealed at the desired temperature could be observed in **Figure. 4**. With the solution-processed AlOx layers annealed at the same temperature, Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices both demonstrated a similar ON/OFF ratio. The most significant difference between Ni/AlOx/Pt and TiN/AlOx/Pt samples annealed at the same temperature was the fluctuation of resistance values at HRS and LRS. Compared with TiN/AlOx/Pt samples, it is noted that resistance values of Ni/AlOx/Pt samples fluctuated with smaller amplitude, which indicated that Ni/AlOx/Pt RRAM devices demonstrated better stability and reliability with the solution-processed AlOx layers. In addition, Compared with TiN/AlOx/Pt RRAM devices, Ni/AlOx/Pt devices with solution-processed AlOx layers annealed at different desired temperatures showed lower operation voltages. For Ni/AlOx/Pt RRAM device, the voltage of Forming operation was very close to those of the following SET operations, which indicated the forming-free characteristic of the Ni/AlOx/Pt RRAM device. Therefore, the power of the first SET for the Ni/AlOx/Pt RRAM device could be considered as the initial power, which was lower than that of the TiN/AlOx/Pt RRAM device. During the following SET operations, Ni/AlOx/Pt RRAM device always showed lower power than that of the TiN/AlOx/Pt RRAM device due to the lower operation voltage (they had the same compliance current of ~ 1mA). The same performance could be also observed during the RESET process.



**Figure 4**. Endurance (a) (c) (e) and retention (b) (d) (f) performance of Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices annealed at 225/250/275°C.

For both Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices, the bipolar RS performance was associated with the switching mechanism based on the formation and rupture of CF in the solution-processed AlOx layer [5, 8, 10-13, 17-24, 26-29]. Compared with active metal materials like Ag and Cu, Ni and TiN have lower metal activity, which indicated that the redox reaction of Ni and TiN is not easy to occur during the SET and RESET process [12, 13, 22-24]. In general, CF comprising oxygen vacancy has been considered to play a decisive role during the switching process [8, 11, 26-29]. We take the Ni/AlOx/Pt RRAM device as an example. **Figure. 5a** demonstrated the initial OFF state of the Ni/AlOx/Pt RRAM device without external bias. When the positive voltage bias was applied onto TE, the oxygen ions (O2-) would be generated due to the combination process of oxygen atoms stayed in the AlOx layer and electrons brought by the external electric field. With the effect of the electric field, the generated oxygen ions drift to TE while oxygen vacancies are left in the dielectric layer, which resulted in the formation of CF [8, 11, 26, 27]. When oxygen vacancies continuously accumulated until the CF connected the TE and BE, the device showed the ON state after the SET operation, as illustrated in **Figure. 5b** [26-29]. Conversely, with the negative voltage bias added onto the TE Ni, oxygen ions stored in TE would move back to the dielectric layer and be transferred back to oxygen atoms, which filled the defect induced by oxygen vacancies and resulted in the rupture of CF. After the RESET operation, the device was at an OFF state, as demonstrated by **Figure. 5c** [4, 5, 8, 11, 26-29].



**Figure 5**. Switching mechanism based on CF of Ni/AlOx/Pt RRAM devices with (a) initial OFF state, (b) ON state after the SET operation and (c) OFF state after the RESET operation.

The electrical characteristics and discussion about the switching mechanism above have indicated that the variation of RS performance between Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices was largely determined by different materials of TE, which might be associated with (△ΦM) between TE and BE [30-35]. The work functions (Φ) of Ni, TiN and Pt are ~5.35 eV, ~4.4 eV and ~5.93 eV, respectively [36-38]. Therefore, the △ΦM for TiN/AlOx/Pt and Ni/AlOx/Pt devices are 1.53 eV and 0.58 eV, respectively. **Figure. 6** showed the energy band diagrams of the Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices with the drift of oxygen ions and electrons. In **Figures. 6a** and **6c**, the oxygen trap stayed in solution-processed AlOx layers of Ni/AlOx/Pt and TiN/AlOx/Pt RRAM devices without external bias, which showed the initial OFF state of devices. In **Figures. 6b** and **6d**, during the formation process of oxygen vacancy conductive filaments after the SET operation with the effect of the external electric field, electrons drift from BE through the dielectric layer and then reached the TE at last. During the drift process, electrons combined with oxygen atoms and then generated oxygen ions while oxygen vacancies stayed in the dielectric layer and then formed the CF. Generally, the definition of work Φ is the minimum energy required for electrons to escape from the inside of the metal into the vacuum, which means that the greater the work function, the more escape energy is required [30-32]. During the whole switching process, the drift process of electrons was influenced by △ΦM between TE and BE [31, 32, 34]. The higher △ΦM indicated that more energy from the electric field was required to support the drift process of electrons from BE to TE [29-32, 34, 35]. Therefore, although the solution-processed AlOx layers were fabricated under the same conditions, it was necessary for TiN/AlOx/Pt to presented the completed RS performance with a higher operating voltage. Reversely, due to the smaller △ΦM between Ni and Pt, less energy was required during the movement of electrons. Therefore, Ni/AlOx/Pt showed lower voltages during the SET process. When the negative voltage bias was applied onto TE Ni, less energy was needed to cancel the band bending of the AlOx layer, which indicated lower voltage during the operation process.



**Figure 6**. Schematic of energy band diagrams during the SET process of metal TE/AlOx/Pt RRAM devices with TE Ni and TiN under no bias (a) (c) and positive bias (b) (d).

**Conclusions**

All TE/AlOx/Pt RRAM devices with solution-processed spin-coated AlOx layers annealed at various temperatures (225°C/250°C/275°C) demonstrated typical bipolar RS characteristics with the external voltage bias. All operation voltages were lower than 4 V and the lowest one was ~ 1V while the ON/OFF ratio was larger than 103 which indicated the excellent RS performance of the solution-processed AlOx layer. Compared with TiN/AlOx/Pt RRAM devices, lower operation voltage and lower energy consumption were obtained on Ni/AlOx/Pt RRAM devices due to the △ΦM between Ni and Pt was lower than that between TiN and Pt.

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