Memristive Behaviour of Ag-doped-HfO\textsubscript{2} Thin Films Prepared by Magnetron Sputtering

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Abstract. The bipolar resistive switching is suitable for the applications of information storage, logical operation and neuromorphic computation. This paper reports the bipolar resistive switching behaviour in HfO\textsubscript{2}:Ag-based memristive device. Under DC sweeps, the Ag/HfO\textsubscript{2}:Ag/p\textsuperscript{++}-Si device showed a uniform bipolar resistive switching feature with a resistance ratio of \sim 15. Moreover, in the low voltage sweeping region, the device showed analog resistive switching behaviour with gradual SET and gradual RESET characteristics. It is suggested that the formation/rupture of Ag-filament is crucial in the resistive switching, and the gradual changes in resistance might have resulted from the dissolution of Ag atoms from active Ag top electrode (TE) rather than only from local migration of Ag atoms inside the dielectric layer. This new memristor structure with the analog resistive switching is expected for the future application of memristor as a nonvolatile memory and neuromorphic computing.

1. Introduction

Memristors and their functionalities have now become a vital research interest of researchers in the field of advanced electronic devices for a new type of information storage device and computing systems [1]. In 1971, for the first time, memristor became part of the circuit theory [2]. However, until the discovery of the memristor in 2008 [3], it has only remained a mere theoretical concept. A memristor device is defined as a device that can change its resistance to a flowing charge. This kind of device is especially applicable to many applications in electronics, including neuromorphic computation, logic and analog operations, neural networks and pattern recognition [4]. The resistive random-access memory (RAM) belongs to the family of the memristors with a switchable resistance by a voltage. In recent years, various groups of researchers have given attention intending to understand the mechanisms involved in the switching process in RRAMs [5][6]. One of the most widely discussed questions is the improvement of the switching characteristics in metal oxides such as the ON/OFF resistance, switching speed, extreme endurance (>\textsuperscript{12} cycles) and low operating voltage and power [7].

A memristor is formed by sandwiching of semi-conductive or dielectric materials thin layers between metal electrodes exhibiting charge-transport characteristics under applied electric-field between two electrodes. In order to realize the memristive characteristics in memristor devices, different kinds of metal oxides, chalcogenides [8][9][10] have been investigated. It has been experimentally demonstrated that the resistive switching behaviour in a memristor device can be ascribed by the migration of oxygen vacancies or metal ions. When an electrical voltage is applied to
the memristor device, these oxygen vacancies or metal ions formed conductive path across the electrodes, which is called “conductive bridge or filament (CF).” Unlike the formation of CF, when an electrical voltage is applied with opposite polarity, the subsequent broke down of that CF is observed during a switching operation. In respect to the practical applications, during formation and rupture of CF, a low-resistance state (LRS or On-state) and high-resistance state (HRS or Off-state) can be achieved. If during switching operation, On/Off ratio more than ~10 is sufficient to store the information with a less error. It is known that memristor if metal ion (such as Ag⁺, Cu²⁺ etc.) are involved in switching operation of memristor usually exhibits an unstable performance due to the irreversible migration of these ions. Because of this discrepancy, the metal-CF based memristive devices, have not yet met the performance requirements in terms reliability and stability for their practical device applications. Considering such challenges, selection semi-conductive or dielectric materials as sandwiched layer and electrodes materials are very more important aspects to optimize the design of device and to achieve the performance for industrial level production. Moreover, the design of memristor device and materials properties are considered vital for artificial electronic synapse or in neuromorphic engineering.

Among the number of materials previously studied, HfO₂-based resistive switching devices are of special concern because they have been incorporated into modern CMOS technology. As a result, HfO₂-based memristors have been widely investigated for nonvolatile memory applications [11]. In this work, Ag-doped HfO₂ films (named as HfO₂:Ag composite films) have been fabricated by sputtering. By using this composite films, we have designed and fabricated memristor devices as of Ag/HfO₂:Ag/P⁺⁺-Si structure and demonstrated the memristive behaviour that can gradually be modulated by using positive/negative pulse train. This gradual increase/or decrease in conductance of memristors is very crucial to realize the various bio-synapse function and its applications.

2. Experimental Detail

Figure 1 shows that a memristor device was designed by using a HfO₂:Ag (200 nm) thin layer sandwiched between Ag(100 nm) as top electrode (TE) and p⁺⁺-Si as a bottom electrode (BE). The p⁺⁺-Si (15×15 mm²) BE are cleaned by using a standard RCA method. First, a HfO₂:Ag thin layer was deposited p⁺⁺-Si on by sputtering using a HfO₂ target with Ag small slices placed on it. After that, an Ag thin film is deposited using pure Ag target and photolithography and lift-off technique Ag electrodes are patterned on HfO₂:Ag. All of the film’s deposition processes were taken placed in Ar environment as sputtering gas at room temperature. The power source Keithley 2636B was used to analyze the electrical characteristics of the device.

![Figure 1. Illustration of Ag/HfO₂:Ag/p⁺⁺-Si memristor with electrical measurement configuration.](image)

3. Results and Discussion

In order to measure the current-voltage (I-V) characteristics, a positive or a negative biased voltage is always applied to the Ag TE of Ag/HfO₂:Ag/p⁺⁺-Si memristor device. All the voltages are applied on the Ag top electrode (TE) while the bottom electrode (BE) p⁺⁺-Si is grounded. Figure 1(a) shows the I-V curve of an Ag/HfO₂:Ag/p⁺⁺-Si memristor device. The voltage bias from 0 V to 3.5 V, from 3.5 V to -3.0 V and from 3.0 V to 0 V to analyze the I-V characteristics. The biased voltage increases and decreases by small sweeping steps of 20 mV. The I-V curve is showed a hysteresis loop that indicates the typical memristive features [12] and the gradual increase in current with voltage is indicated a
typical analog resistive switching characteristic, as well. It is observed that during the positive biased voltage, the current increases gradually and the devices the resistance state is switched to LRS from HRS, called “SET” operation. After the SET operation, upon negatively biased TE, the current decreases gradually, and resistance state switched to HRS from LRS, called “RESET” operation. The ratio $R_{\text{On}}/R_{\text{Off}} \sim 15$ is enough to realize the memory applications. Moreover, the cumulative distribution function (CDF) percentage of $R_{\text{On}}$ and $R_{\text{Off}}$ showed in figure 2(b) for 100 cycles is represented close window which is an adequate level of uniformity.

Figure 2. (a) Electrical characterization of Ag/HfO$_2$:Ag/p$^{++}$-Si structure. (a) I-V curve; (b) CDF (%) of HRS and LRS for 100 consecutive cycles.

The positive region of I-V curve and it’s linear fitting results are plotted in figure 3(a) to understand the charge transport characteristics in Ag/HfO$_2$:Ag/p$^{++}$-Si memristor. At HRS, the I-V curve in the low-voltage region exhibits linear behaviour ($I \propto V$) which indicates an Ohmic behaviour and a nonlinear change ($I \propto V^2$) in resistance followed by a steep current is realized in high voltage region. Such type of charge transport behaviour at HRS could be explained by the space charge limited current (SCLC) mechanism [13]. At HRS, the linear I-V curve shows that conduction is dominated by thermally generated carriers followed by a rapid increase in current which could be resulted from charge carriers absorbed in traps originated from the doping of Ag atoms in HfO$_2$ thin film. When biased voltage is increased enough, a sharp increase in current is observed, which could be realized by the formation of CF across the electrodes by electrochemical metallization. It is well known that if charge transport behaviour is governed by SCLC at HRS, the SCLC or Poole-Frenkel emission etc. could be realized in the LRS observed subsequently [14]. At LRS, when biased voltage is decreased, the I-V curve shows a linear behaviour, indicating the formation of Ag-conductive filament.

Figure 3. (a) Demonstration of charge transport and physical mechanism mechanisms. (a) I-V curve plotted in double logarithmic scale; (b, c) schematic illustration of formation/rupture of Ag-filaments.
To demonstrate the physical mechanism involved in this kind of memory device during the switching process and physical model is presented in figure 3(b, c). From figure 3(c), upon a positive bias voltage, the Ag atoms diffused toward the BE through HfO$_2$:Ag thin layer, which are connected the TE and BE. Furthermore, at high voltage region, the surface of Ag TE is oxidized in Ag$^+$ ions. These ions are subsequently migrated toward the BE and subsequently reduced into Ag atoms near the surface of TE. The simultaneous multiple reduction process promoted the growth of Ag-CFs near the TE and BE as well. Figure 2(c) shows that this will consequently result in a change of resistance from HRS to LRS called set process. After this process, if a negatively biased voltage is stressed upon TE, the device achieves HRS from LRS, which might be explained that Ag-CFs are ruptured by Joule heating effect. The doping of Ag atoms in HfO$_2$ thin layer could initiate the formation of Ag-conduction filament (Ag-CF) from TE to BE, resulting in a uniform switching performance.

More interesting, it is observed that the response current consecutively increases or decreases under repeated voltage sweeps in a DC mode, as shown in figure 4. First, a continuous SET process is increased from 2.0 V to 4.0 V by continuously increasing the voltage of non-identical consecutive sweeps, resulting in a gradual increase of conductance. A continuous RESET process is carried out with a consecutive decrease of conductance by gradually adjusting the voltage sweeps of RESET from -2.8 V to -3.5 V. It is worth noting that this type of continuously decreasing or increasing in resistance between these multiple intermediate states is a typical characteristic of analog type of switching. This kind of switching behaviour is distinguishable from the digital type of switching in which an abrupt change will be observed in the resistance state from HRS to LRS under a non-identical sweeping bias. From these results, we can infer that the conductance of the device can be adjusted by modulating the applied electric filed in Ag/HfO$_2$:Ag/p$^+$/Si memory devices. It is noted that although the ratio of $R_{on}/R_{off}$ is only about 15, a reliable and uniform switching can be observed, as shown in figure 2(b). Therefore, it can be assumed that this experimental result might have resulted from the effective confinement of the filament formation/rupture in the Ag/HfO$_2$:Ag/p$^+$/Si memory device. The observed gradual change in conductance might result from more Ag atoms dissolved in HfO$_2$ thin layer, demonstrating well the mechanism in which the cross-sectional size of the Ag-CF is increased rather than the mechanism where a localized trapping and de-trapping conduction is deduced.

![Figure 4](image)

**Figure 4.** Analog switching behaviour of Ag/HfO$_2$:Ag/p$^+$/Si structure. Gradual SET (a) and RESET (b) processes of non-identical consecutive sweeps using a positive and negative biased voltage.

In a bipolar switching process, an HRS/LRS ratio of ~15 can manifest a digital type of switching through the unbridged and bridged Ag-CF filaments across the TE and BE. In contrast, repetitive sweeps under a voltage less than that of SET is not enough for the growth of Ag CF to ultimately bridge the TE and BE. Figure 3(b, c) shows that with increasing bias voltage, Ag atoms diffused and accumulated at the Ag/HfO$_2$ interface and migrated toward the BE from TE. Furthermore, because the slow growth of Ag filaments is responsible for the Ag-CFs growth in Ag/HfO$_2$:Ag/p$^+$/Si memory devices from the active electrode to the counter electrode, a decrease in the effective gap would be promoted between the electrodes unless a negative bias is applied. From the I-V curve, it has is observed that Ag-CFs tend to maintain their original shapes even at minimum biased voltage. Therefore, when the sweep voltages are consecutively increased, it can be expected that the effective...
gap between TE and BE could be decreased and the lateral size of the conducting filaments then might increase, leading to a rise in the current flow, as shown in figure 4 [15][8].

4. Conclusion
In this article, we have fabricated the memristor device as Ag/HfO$_2$:Ag/p$^{++}$-Si structure by the sputtering method. The device has shown a superior bipolar resistive switching characteristic which is suitable for nonvolatile memory devices. The resistance state of the Ag/HfO$_2$:Ag/p$^{++}$-Si memristor can be explained based on the formation and rupture of the Ag conducting path under an electric field. This Ag/HfO$_2$:Ag/p$^{++}$-Si memristive device having analog type of resistive switching functions could provide a new way to develop an analog memory device for neuromorphic system and artificial electronic synapse in the near future.

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6. References
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