Improved Resistive Switching of Ru: SiO$_2$/TiO$_2$ Based Memristive Devices

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Abstract. In this paper, the resistive switching behaviors of Ru:SiO$_2$/TiO$_2$ based memristive devices have been investigated. It is found that the random and uncontrolled formation of conductive filaments in the Ru/Ru:SiO$_2$/p$^{++}$-Si devices are crucial to realize a filamentary resistive switching. It is also found that the resistive switching behavior of Ru/Ru:SiO$_2$/p$^{++}$-Si devices could be significantly improved via inserting a TiO$_2$ interfacial layer as in the form of Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device structure. In the modified device, strong and stable conductive filament formation could be realized when the top electrode is positively biased. In addition to nonvolatile memory applications, an analog-type switching behavior has also been realized in our newly proposed resistive switching device. The current obtained analog conductance modulation is essential for simulating synaptic functions in electronic devices for neuromorphic applications.

1. Introduction
Over the past decade, two-terminal resistive switching (RS) devices have gained considerable research interests because of their simple architectures, enormous potential for next-generation nonvolatile memory technology, and are proved to be an attractive candidate for biologically inspired neuromorphic computing systems $^{[1][2]}$. However, to date, it is still challenging to fabricate an ideal device with excellent performance in terms of reliability and stability as well as low power consumption. Recently, two types of RS devices, such as (i) valence change memory (VCM) and (ii) electro-chemical metallization (ECM) devices, have been extensively investigated.

It is indicated that oxygen ions or vacancies serve as migratory species during the switching process in VCM devices. These devices have a high data retention capability but consume a lot of power due to the relatively high diffusion energy of oxygen in the oxides-based switching layer $^{[3]}$. In contrast, the switching mechanism in ECM devices lies in the redox process and subsequent migration of active metal...
atoms (i.e., Ag \[4\] and Cu \[5\]) into the solid electrolyte layer as well as the corresponding formation of conductive filaments (CFs) when a voltage is applied. It is noted that owing to the diffusion coefficient of active metal ions is higher in the dielectric layer \[6\], there could resulted in a fast migration of metal ions (Ag\(^+\), Cu\(^+\)) and a random growth of CFs, as well as the clustering of metal atoms in the electrolyte layer \[7\]. Therefore, in ECM devices, the repeated switching operation overly expands the area of filaments, which would result in a hard breakdown of devices. These prevailing situations in both VCM and ECM devices are the primary concerns of their industrial applications. Recently, different strategies for improving the RS in ECM devices have been reported, e.g., doping of metal atoms\[8\] and deliberately inserting an additional layer in the metal/insulator/metal \[9\] for controlled filament growth/rupture in the solid electrolyte layer.

In this study, the Ru-doped SiO\(_2\) (Ru:SiO\(_2\)) based RS devices have been fabricated by a sputtering method using Ru and p\(^{++}\)-Si as top and bottom electrodes. The single-layer memristive device structured as Ru/Ru:SiO\(_2\)/p\(^{++}\)-Si demonstrates a typical filamentary switching with a small on/off ratio and poor data retention. However, after inserting an interfacial layer of TiO\(_2\) between Ru:SiO\(_2\)/p\(^{++}\)-Si, the device shows a uniform switching behavior with excellent retention properties. Also, the Ru/Ru:SiO\(_2\)/TiO\(_2\)/p\(^{++}\)-Si device exhibits an incremental conductance, which is essential for various neuromorphic applications. Furthermore, the corresponding switching mechanisms both in Ru/Ru:SiO\(_2\)/p\(^{++}\)-Si and Ru/Ru:SiO\(_2\)/TiO\(_2\)/p\(^{++}\)-Si devices have been discussed in this article.

2. Device Fabrication Methods

Figure 1(a, b) illustrates the configuration of RS devices with the structure of Ru/Ru:SiO\(_2\)/p\(^{++}\)-Si and Ru/Ru:SiO\(_2\)/TiO\(_2\)/p\(^{++}\)-Si respectively. The following procedure was adopted to fabricate these devices: (1) p\(^{++}\)-Si substrates were cleaned with acetone, ethanol, and distilled water for 10 minutes to remove any remaining contaminants; (2) A Ru:SiO\(_2\) layer of 100 nm thickness was deposited via RF sputtering using a SiO\(_2\) target with Ru slices placed on it; (3) A circular hole mask with a diameter of 150 \(\mu\)m was used to form top Ru electrodes directly on the Ru:SiO\(_2\) layer by a DC sputtering process using a pure Ru target. Also, for the improved devices, before the deposition of Ru:SiO\(_2\) layer, a 20 nm thick TiO\(_2\) layer was deposited on the p\(^{++}\)-Si substrate first using a TiO\(_2\) target, and the following steps were the same as above mentioned ones. The whole sputtering process for Ru/Ru:SiO\(_2\)/p\(^{++}\)-Si and Ru/Ru:SiO\(_2\)/TiO\(_2\)/p\(^{++}\)-Si devices was carried out with a deposition pressure of 0.5 Pa under the flow of Ar gas. The electrical measurements were performed at room temperature with a power source (2636B Keithley) hooked with a probe station.

![Fig.1. Schematic of (a) Ru/Ru:SiO\(_2\)/p\(^{++}\)-Si device and (b) Ru/Ru:SiO\(_2\)/TiO\(_2\)/p\(^{++}\)-Si device, respectively.](image)

3. Results and Discussion

The current-voltage (I-V) characteristics of the devices illustrated in Fig. 1 (a, b) are analyzed to investigate the influence of TiO\(_2\) interfacial thin layer in the Ru:SiO\(_2\) based RS device. Fig. 2(a) depicts a typical filamentary RS behavior in Ru/Ru:SiO\(_2\)/p\(^{++}\)-Si device, where set/reset switching is realized at opposing I-V polarities. Subsequently, a histogram shown in Fig. 1(b) and statistical data illustrated in...
the inset of Fig. 2(b) present the cycle-to-cycle variations in set/reset voltages. It can be seen that set and reset voltages broadly vary from +0.4 V to +1.7 V and -0.4 to -1.7 V, respectively. Similar to conventional single-layer SiO$_2$ based RS devices, the variations in the operational voltage of Ru/Ru:SiO$_2$/p$^{++}$-Si device might originate from the random formation of filaments in the SiO$_2$ dielectric. In contrast, it can be seen in Fig. 2(d, e) that the stability of the operating voltages is remarkably improved in Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device. The reset and set voltages range from +0.7 V to +1.4 V and +1.2 V to +1.9 V, respectively, showing that the set/reset voltage is more tightly distributed in the Ru:SiO$_2$/TiO$_2$ bilayer based device than that in the monolayer Ru:SiO$_2$ based device.

It is known that data retention is also a key factor for memory applications. Therefore, the retention properties of above two devices were measured at a constantly applied reading voltage (V$_{\text{read}}$ = 0.5 V), and the data was acquired at certain time intervals (in this study, 100s intervals), as shown in Fig. 2(c, f). It is worthy of noting that the HRS/LRS ratio in the device of Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si is upheld for more than 10$^5$ s (Fig. 2(f)) with no discernible degradation, much longer than that (5×10$^3$s) in the device of Ru/Ru:SiO$_2$/p$^{++}$-Si. The resistance value at LRS is kept stable during the test process. From this, it can be concluded that deliberately inserting the TiO$_2$ layer has improved the RS performance and plays an essential role in the data retention ability of Ru:SiO$_2$/TiO$_2$ bilayer based RS memristive devices.

In order to investigate the RS mechanism in both Ru/Ru:SiO$_2$/p$^{++}$-Si and Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si devices, I-V characteristics are further analyzed. For the device of Ru/Ru:SiO$_2$/p$^{++}$-Si, the fitted results in HRS demonstrate the charge transport behavior following the trap-controlled space charge limited conduction (SCLC) mechanism, which is consist of the Ohmic (slope ~1.1) region, the Mott-Gurney law (slope ~2) region, and the steep current (slope ~8.5) region (shown in Fig. 3(a)). The SCLC, Poole–Frenkel and Ohmic conduction could be realized sequentially in LRS if the trap-filled SCLC dominates the HRS conduction mechanism. A similar phenomenon can be seen for Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device in HRS, while a steep drop in current is observed in LRS, as shown in Fig. 3(b). However, the fitted results of Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device show that the current decreases linearly with the decreasing voltage, and no steep drop in current is observed, indicating the existence
of Ohmic characteristics. Furthermore, the resistances in LRS are also analyzed as a function of temperature (300 to 700 K), as in Fig.3(c) and (d). It is observed that the resistance of the device is increased linearly with temperature, indicating a typical charge transport behavior of metals. For Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device, the temperature coefficient ($\alpha$) is then calculated as $4.13 \times 10^{-4}$ from the linearly fitted data, which is very close to the $\alpha$ value of Ru ($\approx 4.79 \times 10^{-4}$) [13]. From these results, it can be concluded that a strong Ru filament could be formed when the Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device is fully electroformed. Similarly, RS behavior has also been observed in our early research work on Ag:SiO$_2$ based memristive device via inserting TiO$_2$ interfacial layer [14].

Moreover, the physical mechanism involved in RS behavior in Ru/Ru:SiO$_2$/p$^{++}$-Si and Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si devices can also well explained by a physical model, as shown in Fig. 4. It can be seen that when the top electrode of the Ru/Ru:SiO$_2$/p$^{++}$-Si device is positively biased, multiple tiny conductive filaments of Ru are formed in the SiO$_2$ dielectric matrix (Fig. 4(a)). The formation of multiple filaments in SiO$_2$ could have resulted in non-uniform RS behavior, as already discussed. Upon implementation of positive bias on tope electrode, the pre-existence of Ru atoms in SiO$_2$ matrix may be accumulated, resulting in random growth of Ru filament, and the variation in RS might be due to formation of these weak and multifilament (Fig. 4(b)). In contrast, when the TiO$_2$ layer is inserted between Ru:SiO$_2$ and p$^{++}$-Si, strong filaments could be formed (Fig. 4(d)), which results in uniform RS behavior in Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device. Therefore, a uniform set/reset process is realized in the formation and rupture of Ru filaments when positive and negative bias are applied, respectively, to the top electrode of the Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device. During the reset process, the Joule heating effect plays an essential role in drifting the Ru atom towards top electrodes, which results in the initial resistance in HRS. Also, the geometry of conductive filaments is important for the data retention ability of the device. If a stable and robust filament is formed across the electrode, the LRS can be sustained for a longer time. From I-V analysis at LRS regions in both kinds of the devices, the physical model can well explain that the formation of strong filaments with high densities has finally induced a stable and a reliable RS behavior in Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si device.

![Fig. 3. Fitting results from I-V curves of (a) Ru/Ru:SiO$_2$/p$^{++}$-Si and (b) Ru/Ru:SiO$_2$/TiO$_2$/p$^{++}$-Si devices. (c, d)Resistance in LRS v.s. temperature varying from 300 to 700 K in both kinds of devices.](image-url)
consecutive sweeps are studied. Fig. 5(a) and (b) show a noticeable increase and decrease in current flow under repeated positive (1st-4th) and negative (5th-8th) voltage sweeps, respectively, indicating the realization of analog conductance modulation. This result is vital for simulating the synaptic properties for neuromorphic applications of electronic devices [15].

Fig. 4. Growth of highly conductive filaments in Ru/Ru:SiO$_2$/p++-Si and Ru/Ru:SiO$_2$/TiO$_2$/p++-Si devices. (a) As fabricated Ru/Ru:SiO$_2$/p++-Si structure. (b) Growth of multiple highly conductive filaments for RS behavior in Ru/Ru:SiO$_2$/p++-Si device. (c) As fabricated Ru/Ru:SiO$_2$/TiO$_2$/p++-Si structure. (d) Growth of Ru highly conductive filaments in Ru/Ru:SiO$_2$/TiO$_2$/p++-Si device.

Fig. 5. I-V characteristics under consecutive non-identical positive(a) and negative (b)sweeps applied to Ru/Ru:SiO$_2$/TiO$_2$/p++-Si device

4. Conclusion
In conclusion, an effective method is proposed to improve the resistive switching performance of Ru:SiO$_2$ based memristive device via inserting TiO$_2$ dielectric film as an interfacial layer between Ru:SiO$_2$ and p++-Si. A uniform and stable RS behavior is realized in the modified Ru/Ru:SiO$_2$/TiO$_2$/p++-Si device. From charge transport behavior and temperature effect on the LRS of the devices, it is concluded that the controlled growth of Ru filaments in Ru/Ru:SiO$_2$/TiO$_2$/p++-Si device leads to a reduced variation in switching parameters, i.e., set/reset, HRS/LRS, and improves the retention ability in the memristive devices. Moreover, in the Ru/Ru:SiO$_2$/TiO$_2$/p++-Si device, a gradual switching during the set and the reset processes has been achieved for 4 switching windows, indicating the realization of
analog switching behavior. This analog conductance modulation is critical for simulating synaptic properties in electronic devices for neuromorphic applications.

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