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# Impact of dielectric crystallinity on the resistive switching characteristics of $ZrTiO_x$-based metal–insulator-metal devices

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ABSTRACT

Amorphous and crystalline $ZrTiO_x$-based metal–insulator-metal (MIM) devices were used as the platform to investigate the impact of dielectric crystallinity on the electrical performance of resistive memory devices. Without any forming step, bipolar switching behaviors can be found for devices with both types of dielectrics. However, the opposite initial state and current–voltage (I–V) hysteresis direction suggest different conduction mechanisms which are mainly determined by whether grain boundaries exist. Combining grain boundaries with a higher permittivity, devices with crystalline $ZrTiO_x$ show undesirable operation voltage fluctuation, higher current and switching voltage, and worse endurance as compared to its counterparts. On the contrary, devices with amorphous $ZrTiO_x$ are promising in realizing next-generation nonvolatile memory in terms of low operation voltages of ±1.3 V, a tight distribution of operation voltages, high operation speed of 200 ns, a large sensing margin of 218 times, robust endurance up to $10^5$ cycles, and satisfactory retention performance.



## 1. Introduction

Non-stop development of high performance nonvolatile memory (NVM) has always played an essential role to fuel the ever flourishing information technology. However, it is generally perceived that current charge based flash memories are quickly approaching their scaling limits. To overcome the limits, numerous promising technologies have been proposed to enable more Moore and resistive random access memory (RRAM) is one of the most promising nonvolatile memories for next generation electronics. Besides pursuing high-performance RRAM, understanding the impact of dielectric crystallinity on memory device behaviors is important as well since many widely-used dielectrics under investigation will crystallize into a polycrystalline phase [1,2] when process temperature is higher than 600 °C. One of the significant features of a crystalline dielectric is the existence of grain boundaries and how grain boundaries affect the electrical performance has also been discussed in the literature [3]. Even though the existence of grain boundaries has been identified as a critical parameter in determining memory device performance, the mechanism of resistive switching for crystalline dielectric and direct performance comparison between amorphous and crystalline dielectric have been scarcely discussed [4]. To focus on this topic, $ZrTiO_x$-based metal–insulator-metal (MIM) devices were explored in this work and the major reason to adopt $ZrTiO_x$ is the prominent memory performance obtained by $ZrTiO_x$-based metal–insulator-semiconductor (MIS) devices formed on Ge layer [5]. The main contributions of this work are twofold. (1) Providing more insights into the different resistive switching mechanisms between amorphous and crystalline dielectric for RRAM operation. (2) Confirming that amorphous $ZrTiO_x$ outperforms crystalline $ZrTiO_x$ for RRAM applications in terms of lower current, smaller switching voltages and a tighter distribution of operation voltages.

## 2. Experiment

A Ti and Pt bi-layer of 10/35 nm was sequentially deposited on $SiO_2$/Si as the bottom electrode. Next, a 10-nm $ZrTiO_x$ film was deposited by e-beam evaporation at room temperature as the resistance switching dielectric [5]. Prior to the sequential deposition of 10-nm Ti and 35-nm Pt as the top electrode, $N_2$ rapid thermal annealing (RTA) at 600 °C for 60 s was performed on some samples to investigate the impact of dielectric crystallinity on device performance. All the electrical data were measured by devices with area of 150 × 150 μm.

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns for samples with and without annealing. $ZrTiO_x$ without annealing corresponds to amorphous phase since no diffraction peaks are observed. On the other hand, samples with annealing reveal diffractions peaks respectively at 30.8°, 35.6°, 51.1° and 61.0°, indicating the

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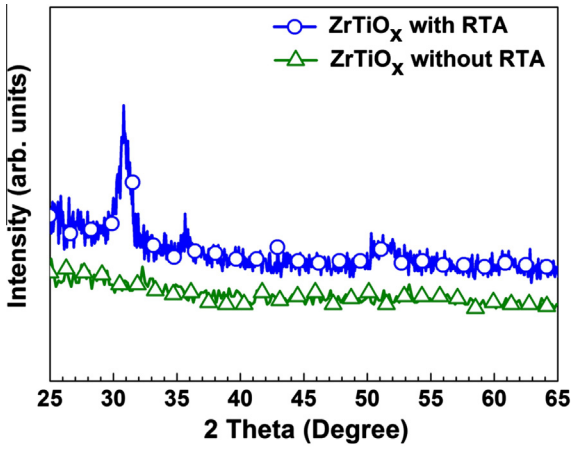


**Fig. 1.** XRD patterns for samples with and without annealing.

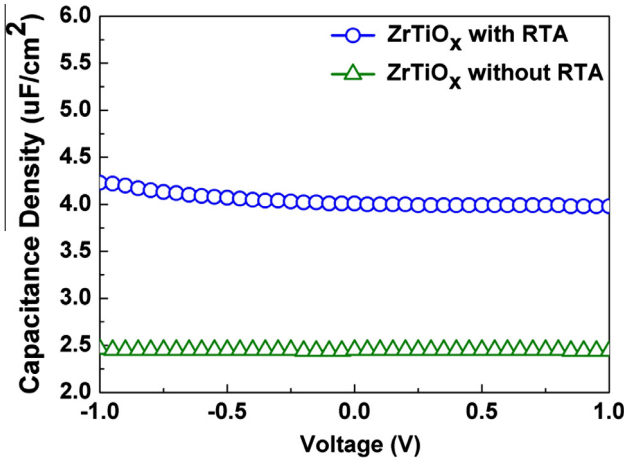


**Fig. 2.** C–V measurement under HRS for devices with and without annealing.

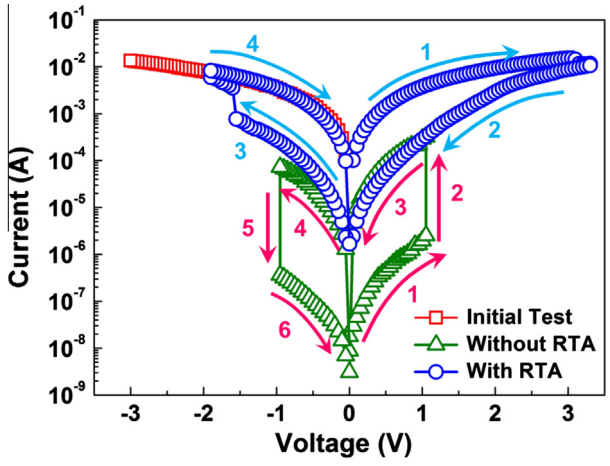


**Fig. 3.** I–V curves for devices with and without RTA. Sweeping from 0 V toward negative bias for annealed devices is also shown.

formation of polycrystalline $ZrTiO_x$ in orthorhombic phase. From the capacitance measurement shown in Fig. 2, it is extracted that the effective κ value of $ZrTiO_x$ would increase from 28 to 46 after crystallization. Note that the κ value includes the effect of the surface Zr-rich $ZrTiO_x$ thin film which was confirmed by Auger electron spectroscopy (AES) for annealed and un-annealed $ZrTiO_x$

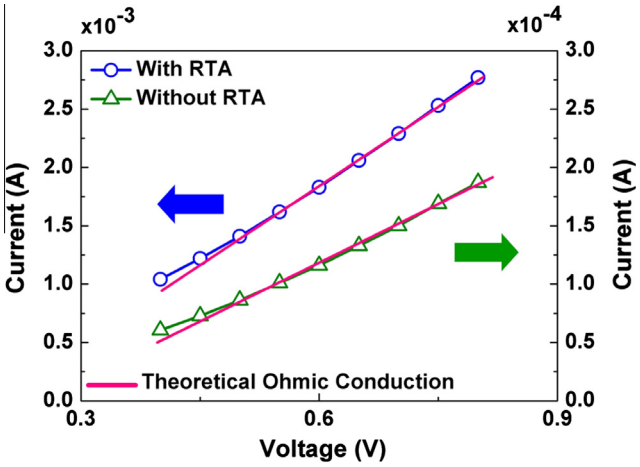


**Fig. 4.** Conduction mechanism at LRS for both types of devices.

(annealed devices have thicker surface Zr-rich $ZrTiO_x$). The formation of the Zr-rich $ZrTiO_x$ thin film is very likely to occur since Ti and Zr are highly reactive in an ambient with $O_2$ even at room temperature [6] due to the large electronegativity difference between Zr (1.33)/Ti (1.54) and O (3.44), making these metals tend to lose their outer electrons. Owing to the additional thermal treatment, the Zr-Rich $ZrTiO_x$ thin film is thicker for samples with annealing. Note that although the annealing was performed in an $N_2$ ambient, the ambient is expected to contain oxygen since the annealing tool is not a vacuum system. Fig. 3 shows the current–voltage (I–V) hysteresis curves for both types of devices. Without a forming step, bipolar resistance switching behavior can be found for devices with amorphous and crystalline $ZrTiO_x$. The switching mechanism for both types of devices can be quite different as evidenced by the opposite hysteresis directions indicated by the arrows. Devices with amorphous $ZrTiO_x$ show initial high resistance state (HRS) and change to low resistance state (LRS) at a SET voltage of 1.0 V. The switching mechanism can be inferred at follows. Because of the supply of electrons near the cathode, reduction of the $ZrTiO_x$ will occur by the reaction $ZrTiO_x + ye^- \rightarrow ZrTiO_{x-y} + yO^{2-}$ (∗) and therefore oxygen ions ($O^{2-}$) can be generated near the cathode. Due to the electric field, the generated $O^{2-}$ near the cathode would drift toward the top electrode and concurrently leave a large number of oxygen vacancies ($V_O^{2+}$). As the number of $V_O^{2+}$ becomes larger, filaments containing oxygen vacancies would extend from cathode to anode and then form LRS. The state change from LRS to HRS can be done by applying a reverse bias to repel $O^{2-}$ into the bulk $ZrTiO_x$ to annihilate the $V_O^{2+}$ in the filaments. On the contrary, devices with crystalline $ZrTiO_x$ show initial LRS and then switch to HRS at a RESET voltage of 3.2 V. The initial LRS is reasonable since the existence of grain boundaries which are oxygen deficient with localized states in the bandgap, assisting electrons conduction through the dielectric [7]. This inference is consistent with the much higher LRS/HRS current as compared to that of devices with amorphous $ZrTiO_x$. As the positive bias increases, due to the reaction (∗), more $O^{2-}$ migrate toward the top electrode through the surface Zr-rich $ZrTiO_x$ thin film. When more oxygen ions are driven into the surface Zr-rich $ZrTiO_x$ thin film, the defects in the thin film will be repaired to form a more robust oxygen-rich film. Once the film is strong enough, it effectively blocks the conduction paths and then the devices switch to HRS [8]. Note that for devices with crystalline $ZrTiO_x$, as the initial sweeping begins from 0 V toward negative bias, LRS fails to switch to HRS since the electric field repels $O^{2-}$ and then Zr-rich $ZrTiO_x$ thin film cannot be repaired. The relatively higher RESET voltage to trigger the HRS may be due to the following reasons. (1) The Zr-rich film is highly