Sol-gel-processed amorphous-phase ZrO₂ based resistive random access memory

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Abstract

In this study, sol–gel-processed amorphous-phase ZrO₂ was used as an active channel material to improve the resistive switching properties of resistive random access memories (RRAMs). ITO/ZrO₂/Ag RRAM devices exhibit the properties of bipolar RRAMs. The effect of the post-annealing temperature on the electrical properties of the ZrO₂ RRAM was investigated. Unlike the ZrO₂ films annealed at 400 and 500 °C, those annealed at 300 °C were in amorphous phase. The RRAM based on the amorphous-phase ZrO₂ exhibited an improved high-resistance state (HRS) to low-resistance state ratio (over 10⁶) as well as promising retention and endurance characteristics without deterioration. Furthermore, its disordered nature, which causes efficient carrier scattering, resulted in low mobility and the lowest leakage current, influencing the HRS values.

1. Introduction

Modeled after the human brain, neuromorphic computing systems have great potential applications in next-generation electronic devices. Neuromorphic computing has emerged as an optimized approach for realizing real-time interaction systems with various environments associated with autonomous applications such as robotics or face classification [1, 2]. However, to realize a neuromorphic computing system using conventional memories and circuits, the scaling issue needs to be resolved. In general, conventional memories and circuits require physical separation between them [3]. Moreover, the neuromorphic computing system requires greater device density to realize human-like operations; therefore, a new device concept, demonstrating extreme scalability, is needed to overcome Moore’s law. A variety of conventional flash memory devices and resistive random access memory (RRAM) devices have been considered promising candidates with extreme scalability (< 10 nm) and improved power consumption efficiency [4–6]. A transistor—one RRAM structure is utilized to solve the sneak path issue while fabricating the RRAM array [7, 8]. According to numerous studies, ZrO₂ is considered a promising active channel layer for RRAM [9–11]. Moreover, the performance of thin-film transistors (TFTs) is remarkably improved using a ZrO₂ insulator for TFTs [12–14]. Thus, ZrO₂ can be simultaneously used as an insulator for transistors and an active channel layer, resulting in reduced manufacturing steps.

The sol–gel process is an easy and simple method to obtain high-quality metal oxide layers. The solution phase precursor allows sufficient amounts of ink for spin-coating, dip coating, and printing processes for large-area applications without using the conventional vacuum-based high-cost deposition tools.

In this study, a sol–gel-processed ZrO₂ layer was used as the active channel layer in RRAM. The structural, chemical and electrical characteristics of the ZrO₂ active channel layers for RRAM were investigated as a function of the post-annealing temperatures (300 °C, 400 °C, and 500 °C). ZrO₂ films annealed at 300 °C
showed an amorphous phase. The RRAM comprising ZrO2 films annealed at 300 °C showed an improved high resistance state (HRS) to low-resistance state (LRS) ratio (>10^6) with promising retention and endurance characteristics. The endurance and retention lasted 10^7 cycles and 10^3 s, respectively, without deterioration. In addition, the 300 °C annealing process has the potential to fabricate flexible ZrO2 RRAM devices on polyimide substrates with high glass transition temperature (311 °C).

2. Methods

2.1. Fabrication process
In this study, 0.001 mol of zirconium (IV) acetylacetonate (Zr(C5H7O2)4) from Sigma Aldrich was used as a precursor. It was dissolved in 9.9 ml of ethanol, and 0.1 ml of ethanolamine (Sigma Aldrich) was added as a capping material. The ultrasonication process was performed for 1 h at room temperature to clear the ZrO2 precursor solution. Commercial indium tin oxide (ITO)-deposited glass substrates (Sigma Aldrich) were prepared to fabricate the ZrO2 RRAM device. Before depositing ZrO2, the substrates were cleaned using ultrasonic equipment for 10 min with acetone and deionized water. UV/O3 treatment was performed for 10 min to eliminate contaminated organic debris and make the surfaces of ITO glass hydrophilic to ensure that the solution precursor was coated appropriately during the spin-coating process. The prepared precursor solution was deposited on ITO glass substrates using a spin-coating method (3000 rpm for 50 s). A soft-drying process at 150 °C for 10 min in air was employed to evaporate the solvent, and additional annealing processes were performed on the hot plates at 300 °C, 400 °C, and 500 °C for 3 h in air. Finally, 20 nm-thick ZrO2 films were formed. A shadow mask was used in the thermal evaporator to form a 30 μm × 30 μm Ag layer, which served as the top electrode, and a 100 nm-thick Ag layer was deposited at a rate of 1 Å s^{-1} while maintaining a pressure of 5 × 10^{-6} Torr.

2.2. Analysis method
The structural features and phase were investigated by measuring the grazing incidence x-ray diffraction (GIXRD) via X’pert Pro with a Cu Kα wavelength of 1.54 Å and a small incident angle of 0.3°. X-ray photoelectron spectroscopy (XPS, Quantera SXM) was used to identify the elemental and chemical compositions. Film thickness was measured using a scanning probe microscope (Park NX20, tapping mode). An Agilent 4155 semiconductor parameter analyzer was run at room temperature to estimate the electrical characteristics of the air.

3. Results and discussions
Figure 1 shows the GIXRD spectra of sol–gel-processed ZrO2 films annealed at 300 °C, 400 °C, and 500 °C. The ZrO2 films annealed at 300 °C did not show any peaks, indicating amorphous-phase ZrO2 films. Films annealed at 400 °C showed only one broad peak at 30.51°, whereas those annealed at 500 °C were consistent with cubic polycrystalline structured ZrO2 films (JCPDS: 81–1550). In detail, a total of four diffraction peaks appeared at 30.51°, 35.17°, 50.77°, and 60.25°, representing the (111), (200), (220), and (311) orientations, respectively. Among them, ZrO2 films primarily grew in the (111) direction. With an increase in annealing temperature, the intensity of the peaks also increased, indicating the enhanced crystallinity and grain growth of the deposited ZrO2 films. Additionally, the preferential orientation peak, particularly for the (111) plane, became sharper and dominant as the post-annealing temperature increased. The Scherrer equation was used to determine the crystalline size; this equation was applied to the full width at half maximum of a peak observed in the GIXRD
where $\lambda$ is the x-ray wavelength, $\beta$ is the width at half the peak value, and $\theta$ is the Bragg angle. The calculated crystalline size of the ZrO$_2$ film annealed at 400 $^\circ$C and 500 $^\circ$C were 2.3 and 13.3 nm, respectively.

Figures 2(a)–(c) shows the O1s XPS spectra of ZrO$_2$ films obtained as a function of the annealing temperature. The O1s spectra have three peaks positioned at 530.0, 531.4, and 532.2 eV, representing three states of oxygen ions. The oxygen ions (O$^{2-}$), called O$_{\text{Lattice}}$, which combined with metal cations and turned into ZrO$_2$, are shown at the 530.0 eV peak. The oxygen vacancies at medium binding energy, called O$_{\text{Vacancy}}$, are signified at the 531.4 eV peak. The peak corresponding to the OH group and/or aqueous molecules adsorbed on the surface of the ZrO$_2$ films is positioned at the 532.2 eV peak. Figure 3(d) shows the area ratio of O$_{\text{Lattice}}$, O$_{\text{Vacancy}}$, and –OH groups as a function of the post-annealing temperature. As the post-annealing temperature increased, O$_{\text{Lattice}}$ started to increase; however, the O$_{\text{Vacancy}}$ and –OH groups started decreasing simultaneously. More oxygen vacancies can be filled by free oxygen atoms from the outside at high temperatures. The dynamic energy of oxygen atoms increased, and they entered ZrO$_2$ and easily filled the oxygen vacancies at elevated temperatures. Finally, they were converted into oxygen ions, combined with metal cations (O$_{\text{Lattice}}$), after cooling.

The I–V curves at different annealing temperatures are shown in figures 3(a) and (b). All ZrO$_2$-based RRAM devices exhibited conventional bipolar characteristics. Initially, the fabricated ITO/ZrO$_2$/Ag devices were in a HRS. When voltage was applied from negative (−10.0 V) to positive (+7.0 V), the current increased abruptly at approximately +2.0 V, and the devices entered a LRS. The voltage at which the current suddenly increases is called the SET voltage. In contrast, when a negative voltage bias was applied from +7.0 V to −10.0 V, the current decreased suddenly, turning into HRS. Binary metal oxides, such as Nb$_2$O$_5$, TiO$_2$, and ZrO$_2$, exhibit resistive switching memory behavior, originating from the formation and destruction of a conductive path with two representative mechanisms: (1) oxygen vacancy-based conductive path within the active metal oxide layers and (2) metallic conductive path formation, originating from oxidation and reduction processes from electrochemical metal electrodes such as Ag or Cu. In this study, the primary mechanism is the metallic conductive path formation, which originates from the oxidation and reduction processes from the top Ag electrode. When voltage was applied from negative (−10.0 V) to positive (+7.0 V), Ag at the interface between the top Ag electrode and ZrO$_2$ films started to oxidize and diffused into the ZrO$_2$ films, resulting in conductive Ag filament formation. The formed Ag filament contacts the bottom ITO electrodes, changing the resistance states from HRS to LRS. Alternatively, when a negative voltage bias was applied from +7.0 V to −10.0 V, the
previously formed conductive Ag filaments were broken by the reduction process and the resistance state returned from LRS to HRS.

Figure 3(c) shows the SET and RESET voltages as a function of post-annealing temperature. The SET and RESET voltages for the amorphous-phase ZrO$_2$ samples annealed at 300 °C are higher than those of the polycrystalline phase ZrO$_2$ samples annealed at 500 °C. Based on the GIXRD data, the ZrO$_2$ films annealed at 300 °C were amorphous, whereas those annealed at 500 °C were polycrystalline. Normally, the grain boundary accelerates ion migration that decreases the SET voltage [15]. In addition, larger grains and fewer grain boundaries reduced the Ag filament formation, making the Ag filament easy to break and lowering the RESET voltages. Therefore, the SET/RESET values of the RRAM comprising amorphous-phase ZrO$_2$ annealed at 300 °C were the highest.

Figure 3(d) shows the HRS and LRS values of fabricated ZrO$_2$ RRAM devices. The HRS/LRS ratios at 400 °C and 500 °C were approximately $10^3$ and $10^1$, respectively. However, at 300 °C, a substantial HRS/LRS ratio of $>10^6$ is observed. It is well known that oxygen vacancy (O$_{V}$) can intensify the leakage current [16]. O$_{V}$s are generally regarded as defects in the oxide that act as traps and enable trap-assisted tunneling or hopping mechanisms, thereby boosting the leakage current phenomenon. However, the RRAM based on ZrO$_2$ annealed at 500 °C showed the lowest HRS values and the largest leakage current, while the O$_{V}$ concentration was the lowest based on XPS analysis. ZrO$_2$ film phase plays a critical role in the leakage current mechanism. Compared with the ZrO$_2$ films annealed at 400 °C and 500 °C, the ZrO$_2$ films annealed at 300 °C showed an amorphous phase. The carrier’s disordered nature and efficient scattering lead to low carrier mobility and the lowest leakage current, influencing the HRS values [17–19].

The J–V relationship was investigated to explain the current conduction mechanism of Ag/ZrO$_2$/ITO devices as a function of the post-annealing temperature. The positive and negative regions of the double logarithmic plot of the J–V curves are shown in figure 4. Furthermore, the relationship between the current and bias voltage of the LRS and initial HRS was linear, followed by the Ohmic conduction based on the following equation:

$$J = \frac{q n_0 \mu V}{d}$$

where q is the elementary charge, $n_0$ is the carrier concentration, $\mu$ is the carrier mobility, and d is the thickness of the ZrO$_2$ layer. In an HRS, the slope of the double logarithmic plot changed from 1 to 2 as V increased. In other metal oxide RRAM devices, the initial transport mechanism was Ohmic, followed by the Child’s square law region, where the current is proportional to $V^2$. Additionally, the Poole–Frenkel (P–F) emission mechanism is dominant during the transition from HRS to LRS. For reference, equation (2) is a P–F emission formula, and the linear section follows P–F emission by fitting ln($J$/$E$) versus $E^{0.5}$.

![Figure 3. J–V curves for (a) the Ag/ZrO$_2$/ITO RRAM devices depending at different annealing temperatures on a linear scale and (b) the Ag/ZrO$_2$/ITO RRAM devices on the log scale. (c) SET/RESET ratio values. (d) HRS/LRS ratio values. (measured device size: 30 $\mu$m × 30 $\mu$m, read voltage: +0.1 V.)](image)
where q is elementary charge, \( \mu \) is the electron’s mobility due to drift, \( N_C \) is the density of states inside the conduction band, E is the electrical field, \( \phi_T \) is the potential energy due to traps or defects, \( k_B \) is the Boltzmann constant, T is the temperature [K], and \( \varepsilon_d \) is the dielectric constant inherent to ZrO₂ [20]. The fitting of \( \ln(J/E) \) versus \( E^{0.5} \) reveals that the P–F transport mechanism is the primary transport mechanism under the HRS condition, regardless of post-annealing temperatures.

Retention and endurance are usually measured to verify the performance of the Ag/300 °C annealed ZrO₂/ITO RRAM device, which has the highest HRS/LRS ratio. The HRS and LRS values were obtained at a
read voltage of +0.1 V. The HRS/LRS ratio (over 10⁶) of the RRAM based on ZrO₂ annealed at 300 °C were the highest and lasted for up to 10⁶ programs/erase cycles. Moreover, the LRS and HRS lasted for approximately 10⁴ s, with minimal degradation.

4. Conclusion

In this study, a ZrO₂ RRAM device was fabricated using the sol–gel method and devices with the best characteristics were studied by varying the annealing temperature. The ZrO₂ films annealed at 300 °C showed an amorphous-phase ZrO₂. RRAM based on amorphous-phase ZrO₂ shows an improved HRS/LRS ratio (> 10⁶) with promising retention and endurance characteristics. Its endurance and retention lasted for 10⁴ cycles and 10⁶ s, respectively, without deterioration. The disordered structures of the amorphous materials lead to low carrier mobility and the lowest leakage current, thereby influencing the HRS value.

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Data availability statement

No new data were created or analysed in this study.

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