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Gd doping improved resistive switching characteristics of TiO_2-based resistive memory devices

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1. Introduction

The resistive random access memory (RRAM) based on resistance switching effect has been extensively studied due to its excellent characteristics of low-power, high-speed operation, nonvolatility, and high-density integration [1-2]. Recently, great efforts have been exerted to investigate two-terminal resistive devices based on binary metal oxides such as TiO_2, NiO [3-4]. Binary metal oxides have simple structures and are compatible with conventional CMOS processing. However, broad dispersions of resistive switching parameters such as V_{set} and V_{reset} are generally observed with continuous resistive switching in memory devices. Here, V_{set} and V_{reset} are the required voltages for resistive transition from high resistive states (HRS) to low resistive states (LRS) and vice versa. The uniform resistance switching characteristics are required for the real nonvolatile memory applications.

In this paper, we report the improved resistive switching characteristics of TiO_2-based memory devices by doping Gd in TiO_2 thin films, which could be attributed to the enhanced formation and rupture effect of the conducting filaments consisting of oxygen vacancies in the Gd-doped TiO_2 films.

2. Experimental

In this study, metal-oxide-metal (MOM) capacitor samples with the structure of top electrodes (TE)/Gd-doped TiO_2 (or TiO_2)/Pt/Ti/SiO_2/Si were fabricated. A 100-nm Pt bottom electrode with a 50-nm Ti adhesion layer was grown by sputtering on SiO_2/Si substrates. Subsequently, Gd-doped TiO_2 （the molar ratio of Gd:Ti is 3:97）and pure TiO_2 oxide films were deposited by sol-gel method on Pt/Ti/SiO_2/Si, respectively. Then a furnace annealing process was performed at 450℃ in a mixing atmosphere of 25% oxygen-nitrogen flowing for 1 h. Finally, the metal W pins of the probe-station were directly applied on the oxide films as the top electrodes. The electrical properties were measured between two top electrodes, equivalently measuring two capacitors in series.

The film thickness is determined by the cross-sectional scanning electron microscope (SEM) image and it is approximately 40 nm in this study. The crystal structures of oxide films are investigated by X-ray diffraction (XRD). Photoluminescence (PL) spectra were recorded at room temperature to investigate the defect states in the oxide films. I-V characteristics of the memory devices are measured at room temperature with an Agilent 4156C in voltage sweep mode.

3. Results and discussion

Fig.1 shows the XRD patterns of the oxide films. Both Gd-doped TiO_2 and TiO_2 are polycrystalline anatase films.

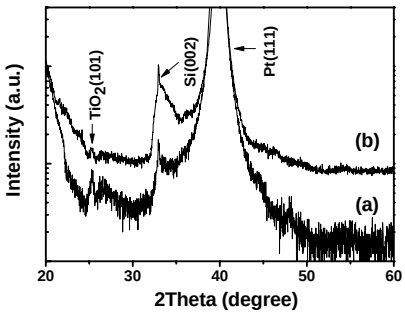

Fig.1 XRD patterns of Gd-TiO_2 (a) and TiO_2 (b) thin films.

There are no evidences for Gd or Gd oxides phases for the Gd-doped TiO_2 films, suggesting that Gd may substitute for Ti positions without changing the anatase structure of TiO_2.

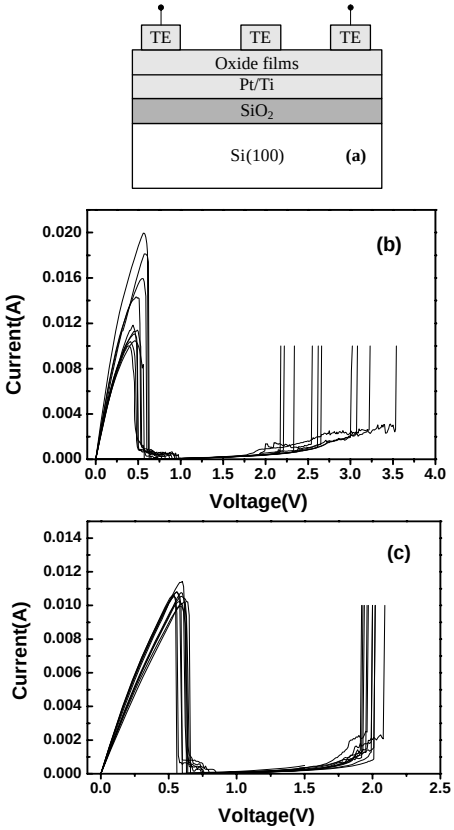

Fig.2 The schematic structure of memory devices (a), the switching I-V curves in TiO_2 (b) and Gd-doped TiO_2 (c) memory devices. The data are from continuous switching of 10 times.

I-V characteristics are recorded in the dc voltage-sweep mode in the positive voltage region. The current compliance is set to 10 mA. Fig.2 (b) and (c) show

the I-V curves in TiO_2 and Gd-doped TiO_2 memory devices, respectively. All the devices reveal high initial resistances and an electroforming process is necessary. Resistive switching from HRS to LRS is induced by increasing the voltage up to a value slightly higher than V_{set}, where an abrupt increase in current appears. Subsequently, sweeping the voltage up to a value slightly higher than V_{reset}, a sudden decrease in current is observed, indicating the resistive switching from LRS to HRS. It is clearly noticed that Gd-doped TiO_2 memory devices show uniform resistive switching compared with TiO_2 memory devices.

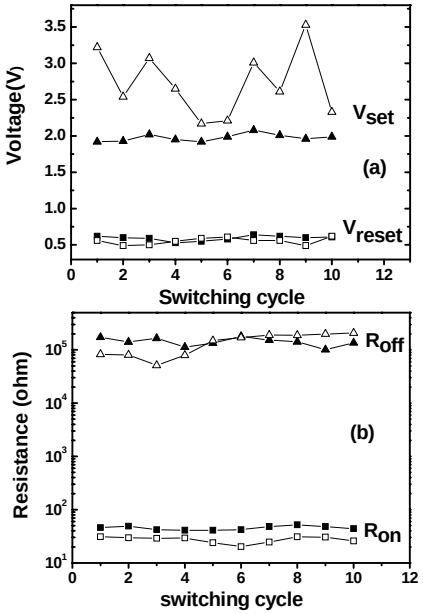

Fig.3 Variation of the resistive switching parameters with respect to the switching cycles in TiO_2 (unfilled) and Gd-doped TiO_2 (filled) memory devices. In (a) triangle (square) symbols represent V_{set}(V_{reset}) data. In (b) triangle (square) symbols represent R_{off} (R_{on}) data. R_{on} and R_{off} are resistances measured at o.2V.

Fig.3 plots the variation of switching parameters, V_{set}, $V_{reset,}$ R_{on} (the resistive values in LRS) and R_{off}(the resistive values in HRS) with respect to the switching cycles. The improvements are evident especially in dispersions of V_{set}. For the Gd-doped TiO_2 memory devices, V_{set} is at 2.0V and V_{reset} is at 0.6V. Both V_{set} and V_{reset} show small random variations in a range of 0.1V. However, for the TiO_2 memory devices, V_{set} has a big random variation from 2.2 to 3.5V for ten switching cycles. In addition, V_{set} of the Gd-doped TiO_2 memory devices is lower than that of the TiO_2 memory devices, which is helpful to decrease the power dissipation in the memory device. It is also found from Fig2(b), the resistance ratio between R_{on} and R_{off} is over three orders of magnitude in all the memory devices. A stable resistance ratio is observed up to ten switching cycles in the Gd-doped TiO_2 memory devices.

The conducting filament model has been proposed to explain the resistive switching of TiO_2 films [5, 6]. In this model, the generation and rupture of conducting filaments are responsible for the LRS and HRS, respectively.

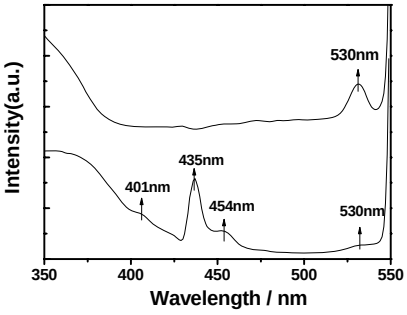

Fig.4 PL spectra of Gd-TiO_2 (a) and TiO_2 (b) thin films measured at room temperature. The wavelength at 530nm corresponds to the defect level for oxygen vacancies [7]. Others are attributed to C.U.S ions and the Frank-Condon principle.

The filament is thought to be one specific form of extended defects in oxide films, such as oxygen vacancies. Fig.4 shows the PL spectra of Gd-doped TiO_2 and TiO_2 films. PL results show that 3%Gd doping don't create new defect energy level in the TiO_2 band gap, but cause the increment of defect state density of oxygen vacancies. Gd doping can induce uniform resistive switching in TiO_2 memory devices. It suggests that Gd dopant plays a role in enhancing the formation and rupture effect of the conducting filaments consisting of oxygen vacancies. However, the improvement mechanisms of Gd doping on the resistive switching of TiO_2 memory devices are not fully understood at present stage and further studies are ongoing.

4. Conclusions

The improvements of resistive switching characteristics of TiO_2 memory devices are obtained by doping Gd in TiO_2 films. The Gd-doped TiO_2 memory devices show uniform resistive switching behaviors including V_{set} of 2.0±0.1V, V_{reset} of 0.6±0.1V, and a stable resistance difference by over three orders of magnitude.

Acknowledgements

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