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# La/Al-doped $ZrO_2$ Thin-Film Resistive Random Access Memory Devices by Sol-gel Method for Transparent Solid-State Circuit Systems

Yiran Wang, Bing Chen, Bin Gao, Lifeng Liu*, Jinfeng Kang
Institute of Microelectronics, Peking University, Beijing 100871, China
*Email: lfliu@pku.edu.cn

**Abstract**

**A sol-gel method with doping technology is conducted in fabricating fully transparent resistive random access memory (TRRAM) devices with configuration of FTO/doped $ZrO_2$/ITO. Sol-gel-derived lanthanum (La) or aluminum (Al) doped zirconium dioxide ($ZrO_2$) film and indium tin oxide (ITO) film were deposited on fluorine tin oxide (FTO) glass substrate and resistive switching (RS) layer successively. Compared with our previous work, doped $ZrO_2$ enhanced the RS uniformity and retention, indicating great application potential for transparent electronic system.**

## 1. Introduction

Transparent solid-state circuit systems, regarding as the next-generation circuits, have been widely studied over the past years[1]. As crucial parts, traditional memory modules tend to be difficult in realizing transparency. Oxide-based resistive random access memory (RRAM), with outstanding electronic performances, reveals its feasibility. Although traditional fabricating processes, such as chemical vapor deposition, atomic layer deposition and sputtering[2] could also fabricate thin-film, sol-gel method highlights itself with low cost and large-area manufacturing possibility. In our previous work, pure $ZrO_2$ thin-film based RRAM suffered from poor uniformity, which remains to be settled. A doping method applied in sol-gel technology for oxide-based RRAM proves to be possible in improving the uniformity[3], and retention enhancement had also been detected.

In this paper, we fabricated La/Al-doped $ZrO_2$ transparent RRAM,with a configuration of FTO/doped $ZrO_2$/ITO under solution process. Thin-film layers including resistive switching (RS) layer and indium tin oxide (ITO) films, being as top-electrode layer, were spin-coated on fluorine tin oxide (FTO) glass substrate by sol-gel method successively. Electronic characteristics of resistive switching were investigated.

## 2. Experiment

A schematic view of FTO/doped $ZrO_2$/ITO TRRAM is shown in fig.1 a), and fig.1 b) shows the fabricated device placed on logo. A doped $ZrO_2$ layer with a thickness of 20 nm was deposited on FTO glass substrate. The process of fabricating RS layer was presented in fig.2(a), where zirconium n-butoxide and lanthanum nitrate hydrate or aluminum nitrate nonahydrate were chosen as precursor materials[4].After mixing and stirring zirconium n-butoxide solution with anhydrous ethanol, the doping salts was added. Acetylacetone and acetic acid, selected as stabilizer, were dipped in the solution above successively. The molar ratio of zirconium butoxide : lanthanum/aluminum nitrate: anhydrous ethanol :acetic acid is 50:1:800:200[5], which means atomic ratio of Al or La to Zr is 2%. Top electrodes with a thickness of 20nm shown in fig.2(b) were fabricated on RS layer. Indium nitrate hydrate and tin chloride pentahydrate were selected as precursor materials[6]. Acetylacetone was acting as stabilizing material. Usually, the molar ratio of indium : tin : acetylacetone is 10:1:30. Being spin-coated and heated, devices were followed by annealing at 500 °C for 2h. Current-voltage measurements were conducted by KEITHLEY 4200 semiconductor parameter analyzer.

## 3. Results

The RS behaviors of this transparent RRAM were tested, as illustrated in fig.3 ,where I-V curves of $1^{st}$, $10^{th}$ and $100^{th}$ were presented. Forming voltage of 8.86V(La) and 7.89V(Al) was observed when turned from initial resistance state (IRS) to low resistance state (LRS). The device turned from LRS to high resistance state(HRS) while negative voltage sweeping was applied. Subsequent voltage sweeping mode was repeated by 0V→3V→0V→3V. Current compliance (CC) of 10mA was fixed. After switching for 100 times, the distribution of $V_{set}$ and $V_{reset}$ was arranged, as manifested in fig.4 comparing with un-doped ones[7]. Operation voltage could be less than 3V, as Table I reveals the characteristics of $V_{set}$ and $V_{reset}$ for both doped devices.

Compared with our previous work[7] , after doping La/Al into $ZrO_2$, the memory window was dropped. As illustrated in fig.5, after switching for more than 100 cycles, the resistance HRS/LRS ratio was more than 5 with no obvious degradation. The RS uniformity was improved like what compares in Table II and fig.5. The retention time of La-$ZrO_2$ and Al-$ZrO_2$ based devices was more than 4000s and 3000s respectively at room temperature as shown in fig.6, which was improved when comparing with un-doped ZrO2 sol-RRAM devices with a retention time of 1000s. This result indicated the potential of doped ZrO2 for storing data.

The reduction of HRS/LRS ratio and uniformity improvement may attribute to the decrease of forming energy of oxygen vacancy (*Vo*) caused by trivalent dopant, since *Vo* mostly formed near dopants in stabilizing the formation of *Vo* conducting filaments. The reduction of resistance is also related to trivalent dopant. The result is in accordance with our previous work[3].

## 4. Conclusions

A doping technology for oxide-based TRRAM by sol-gel method is presented. Top electrode layer and RS layer were fabricated by spin-coating. Fully transparency and bipolar RS behaviors were obtained. Programming current is less than 10 mA and operation voltage is less than 3V. Since doped $ZrO_2$ improved the RS uniformity and retention, this TRRAM has potential applications in large area and transparent electronic system.


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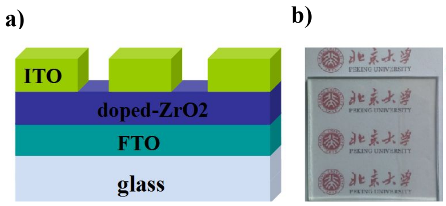


Fig.1 a) Structure of sol-gel based ITO/doped-ZrO2/FTO TRRAM. b)Photograph of fabricated device.

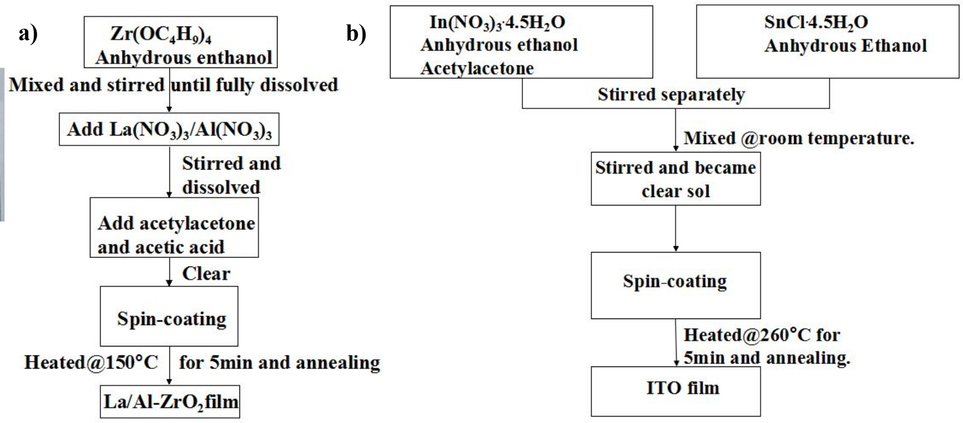


Fig.2 Preparing steps by sol-gel method of a)La-$ZrO_2$ or Al-$ZrO_2$ films and b)ITO films.

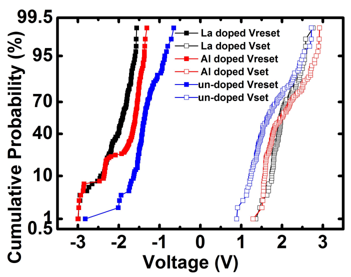


Fig. 4 $V_{set}$ and $V_{reset}$ distribution characteristics for 100 cycles.

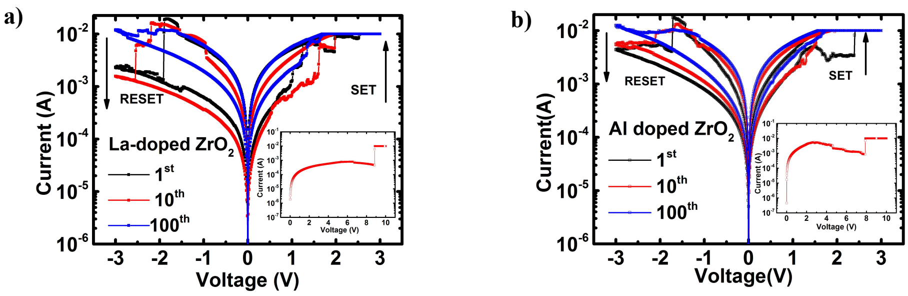


Fig.3 I-V characteristics of a)La-$ZrO_2$ b)/Al-$ZrO_2$ based TRRAM at 1st, 10th, and 100th cycle. The inset shows the forming process for each case.

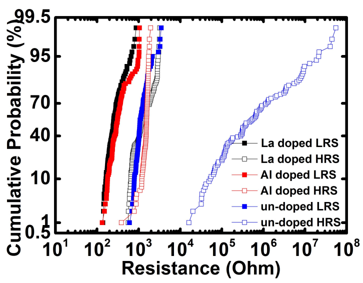


Fig.5 Resistance distribution contrast after 100 cyclings. The doping effect proves improvement in uniformity.

Table I. $V_{set}$ and $V_{reset}$ characteristics for La-doped and Al-doped $ZrO_2$ based TRRAM.

| | range /V | σ/V | μ/V |
|---|---|---|---|
| La-doped $V_{set}$ | 1.4 to 2.9 | 0.29 | 2.03 |
| La-doped $V_{reset}$ | -1.5to- 2.9 | 0.33 | -2.01 |
| Al-doped $V_{set}$ | 1.3 to 2.9 | 0.42 | 2.02 |
| Al-doped $V_{reset}$ | -1.2 to -3 | 0.43 | -1.78 |

σ:standard deviation
μ:arithmetic mean value

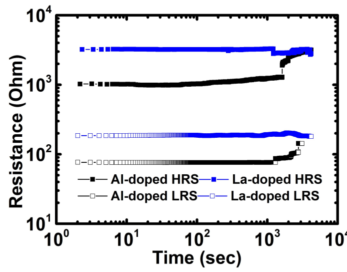


Fig. 6 Retention time of La-doped and Al-doped $ZrO_2$ based TRRAM for more than 4000s and 3000s.

Table II. Standard deviation of HRS and LRS for La-doped, Al-doped and un-doped $ZrO_2$ based TRRAM

| | La | Al | un-doped [9] |
|---|---|---|---|
| $\sigma_{HRS}$ | 828.37 | 242.00 | 10317848.75 |
| $\sigma_{LRS}$ | 167.24 | 241.85 | 638.65 |