Characterization of Oxygen Accumulation in Indium-Tin-Oxide for Resistance Random Access Memory

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***Abstract*— In this letter, we report the oxygen accumulation effect and its influence on resistive switching for gadolinium-doped silicon dioxide (Gd:SiO$_2$) resistance random access memory (RRAM). We find that oxygen absorbance by indium-tin-oxide electrode affects the conduction current mechanism, and remarkably modifies the device performance of RRAM devices. By current fitting, Schottky emission can be observed in both low and high resistance states, from which conduction model is proposed to clarify the oxygen accumulation phenomenon. Reliability tests, including endurance and high temperature retention are further carried out, evaluating the significance of oxygen accumulation effect in redox reaction for RRAM devices.**

***Index Terms*— Oxygen accumulation, indium tin oxide, Schottky emission, RRAM.**

I. INTRODUCTION

RECENTLY, various electronic devices and systems on panel (SOP) technology were widely developed and investigated. For the concept of SOP, amorphous silicon (α-Si) and poly-crystal silicon (poly-Si) thin-film transistors (TFT) [1], [2] for transparent active matrix LCD display and storage devices were widely discussed for the wider application and future development of consumer electronic products [3], [4].

Numerous nonvolatile memories devices such as the ferroelectric random access memory (FeRAM) [5], magnetic random access memory (MRAM) [6], phrase change memory (PCM) [7] and RRAM [8], [9] have been widely investigated for the future applications in portable electrical products. Worldwide researchers have spent great efforts on the investigation of RRAM. Here in this research, we mainly focus on the silicon oxide based system for the advantage of compatibility of low-cost silicon oxide to IC process and its natural stable electrical property. Especially, multiple RRAM working parameters like programming voltage, power consumption and endurance can be effectively improved by combining the metal doping in silicon oxide and the oxygen deficient electrode, which cannot be obtained in the pure silicon oxide RRAM [10], [11].

We applied indium-tin-oxide (ITO), the vastly investigated transparent material, into RRAM and characterized its influence on the redox reaction of resistive switching devices. Specially, we pay attention to the role of indium tin oxide working as the electrode rather than the switching layer, from which we find oxygen accumulation behavior. The accumulated oxygen will affect the conduction mechanism and especially the performance of RRAM device. From our research, we find the electrode influences the device working characteristics and the chemical element composition of the electrode actively affects the RRAM resistive switching behavior.

II. EXPERIMENTAL SETUP

In this letter, the Gd:SiO$_2$ RRAM device was fabricated to investigate the effect of ITO on filament-type RRAM device using metal doped silicon oxide as resistive switching layer. The role of Gd doping is to induce the conductive filament formation in the SiO$_2$ according to our previous study. The Gd co-sputtering with SiO$_2$ was deposited on the patterned TiN/Ti/SiO$_2$/Si substrate with pure SiO$_2$ and gadolinium targets. The switching layer was 20-nm-thick and the sputtering power was fixed with RF power 200W and DC power 10W for silicon dioxide and gadolinium targets, respectively. In addition, the ITO top electrode with a thickness of 200 nm was deposited on Gd:SiO$_2$ film to form ITO/Gd:SiO$_2$/TiN sandwich structure by DC magnetron sputtering. The via

Manuscript received March 8, 2014; revised March 25, 2014; accepted April 8, 2014. Date of publication April 24, 2014; date of current version May 20, 2014. This work was supported by the National Science Council of Taiwan under Contract NSC-102-2120-M-110-001. The review of this letter was arranged by Editor T. San. *(Corresponding authors: T. C. Chang and K. H. Chen.)*

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Digital Object Identifier 10.1109/LED.2014.2316806

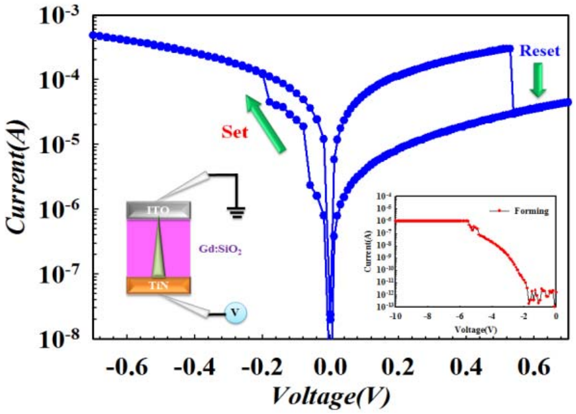

Fig. 1. The typical bipolar switching behavior of the Gd:SiO_2 RRAM devices with ITO electrode. The bottom left and right insets show the schematic measurement method and forming I-V curve, respectively.

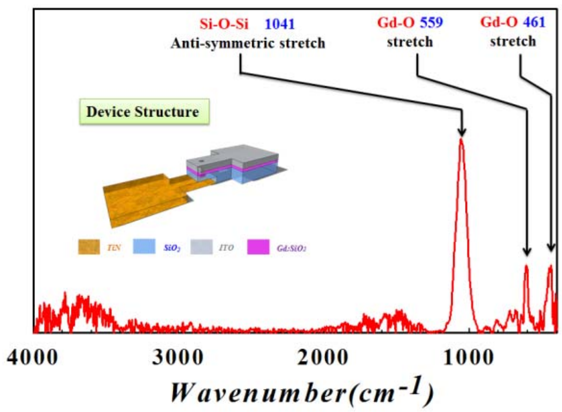

Fig. 2. FTIR spectrum of the Gd:SiO_2 film measured in middle-infrared region. The inset shows the via structure of ITO/Gd:SiO_2/TiN RRAM device.

structure (shown in Fig. 2) is for the strict control of device size and the uniformity of electrical properties. All the electrical measurements were conducted by an Agilent B1500A semiconductor analyzer.

III. Results and Discussion

Before standard electrical measurements, the RRAM devices should be operated with a forming process [8], [9] and the devices were switched from high resistance state (HRS) to low resistance state (LRS) at a voltage of −5.4V with 1μA compliance current (right inset of Fig. 1). The voltage sweep bias was applied on the TiN electrode with the ITO electrode grounded. After that, DC sweeping test was conducted to investigate the influence of ITO top electrode on Gd:SiO_2 RRAM devices, from which bipolar resistance switching characteristics were obtained, as shown in Fig. 1. From the current-voltage curve, a special advantage for the ITO/Gd:SiO_2/TiN RRAM device can be observed, which is the low power consumption. The device can be operated within the small voltage range from −0.7V to 0.7V and Set at merely −0.2V.

In order to confirm the material properties of Gd:SiO_2 thin film, Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical bonding of the Gd:SiO_2 film in this

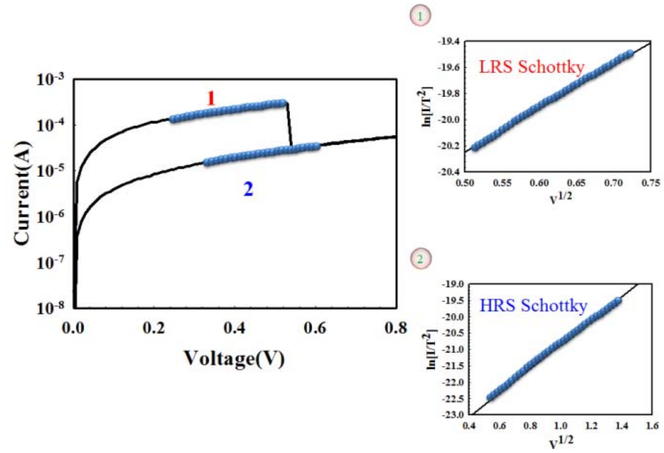

Fig. 3. Conduction current fitting results and the corresponding fitting goodness.

letter. Figure 2 shows that Gd–O stretch bonding was found in the Gd:SiO_2 film at 559cm^{-1} and 461cm^{-1} from FTIR spectrum [12], [13]. These two picks ascribe to the stretching vibrations of Gd-O, this mainly owes to the amorphous film structure fabricated by sputter As the film is not perfect single crystalline structure, the Gd-O chemical bonding is not stress-free type bonding. In addition, the antisymmetric stretch mode of Si–O–Si bonds can be observed at 1041cm^{-1}. According to these absorption peaks expressed in FTIR spectra, we can confirm that the Gd element was bonded with the oxygen element in the SiO_2 film.

To further understand the conduction mechanism, current fittings of LRS and HRS were conducted, as shown in Fig. 3. We can obtain Schottky emission [14] conduction in both HRS and LRS, and the figures in the right side of Fig. 3 are their corresponding fitting goodness. The fitting results imply that the major leakage current originates from the electrons surpassing the potential energy barrier between the interface of the switching layer and the electrode by thermionic effect. Owing to the unequal barrier heights, I-V curve will demonstrate asymmetric property, which can be distinguished from Poole-Frenkel. The device conduction mechanism can be predominantly influenced by the switching layer thickness and the introduction of metal dopants in the switching layer, for this will particularly influence the defects distribution and thus affects the formation of conduction path. Unlike the thick undoped silicon oxide RRAM [15], which needs high operation voltage (-10V–10V) to realize bipolar switch, the Gd doped silicon oxide RRAM can be switched within −0.7V−0.7V for the help of metal ions in the formation process of conduction path.

According to the above-mentioned electrical and material analyses, we propose a model to explain the influence of ITO for the special asymmetric set and reset process in the ITO/Gd:SiO_2/TiN RRAM devices, as shown in Fig. 4. During the set process, the conductive filament grew towards to the ITO electrode by driving oxygen ions to ITO electrode. As lots of oxygen vacancies exist in the ITO thin film, oxygen ions driving force orients to the ITO side. Enhanced by the concentration gradient, together with electrical driving force,

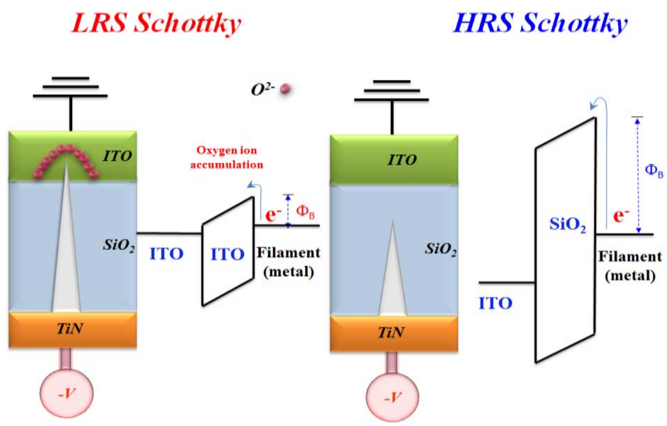

Fig. 4. Conduction model and relative energy band diagrams for LRS and HRS in the ITO/Gd:SiO_2/TiN structure RRAM.

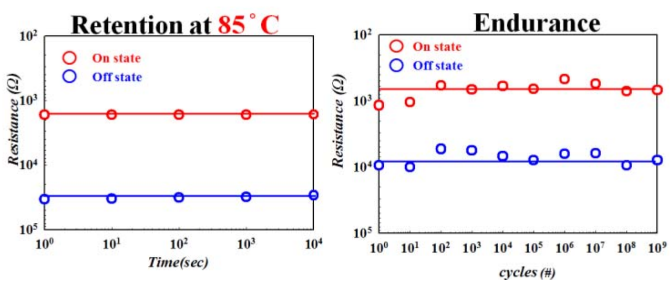

Fig. 5. (a) Retention performance at 85 °C and (b) Endurance properties of Gd:SiO_2 RRAM device. The reading voltage was set as 0.1V.

oxygen ions can be more easily propelled into the ITO electrode, thus we can obtain smaller set voltage compared with traditional single voltage driven force device. The current conduction mechanism in LRS dominated by Schottky emission conduction is due to electron carrier surmounting the barrier height between filament and ITO semiconductor layer. The semiconductor ITO around the filament tip originates from the high oxygen accumulation effect, in which original conductive ITO will be locally oxidized by oxygen ions propelled by the double driving force, which is shown schematically in Fig. 4. This process will results in the ITO energy band-gap widen effect, for the formation of semiconductor-like ITO [16]. As for the reset process, the conductive filament will be oxidized and ruptured, making the current conduction path blocked by silicon oxide. Due to the high energy barrier height of silicon oxide, less carriers can surpass the barrier and thus LRS is switched to HRS. Therefore, the carrier conduction mechanism of HRS in the Gd:SiO_2 RRAM also complies with Schottky emission, originating from carrier overcoming the barrier height between filament and Gd:SiO_2 film, shown in the right diagram of Fig. 4.

To further verify the influence of oxygen accumulation effect on ITO/Gd:SiO_2/TiN RRAM devices, retention and endurance properties were measured. As shown in Fig. 5(a), no significant changes in the resistance values of LRS and HRS were observed even after 10^4 second retention test at 85 °C. The reading voltage was set at 0.1V. Furthermore, the endurance properties were measured by continuous switching cycling as shown in Fig. 5(b). We find the resistance ratio between HRS and LRS remain stable during 10^9 pulse cycling operations. This is the first time for single switching layer silicon oxide based RRAM reaching 10^9 endurance performance, and this also gives us guidance for RRAM performance improvement. By applying ITO, we can utilize the oxygen accumulation effect to better control the reduction and oxidation process.

IV. Conclusion

In conclusion, the influence of oxygen accumulation effect in ITO electrode for bipolar resistance switching properties of the Gd:SiO_2 RRAM devices were investigated and discussed in this letter. Schottky emission conduction in both LRS and HRS are depicted, from which we find the Schottky conduction mechanism originates different barrier height between the filament and electrode. Outstanding performance including stable high temperature retention and 10^9 endurance further unveils the importance for the selection of electrode material, and this also enlightens us one simple way to manipulate oxygen ions in resistive devices.

Acknowledgment

This work was performed at National Science Council Core Facilities Laboratory for Nano-Science and Nano-Technology in Kaohsiung-Pingtung area, NSYSU Center for Nano-Science and Nano-Technology.

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