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Characteristics and Mechanisms of Silicon-Oxide-Based Resistance Random Access Memory

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***Abstract*—Traditionally, a large number of silicon oxide materials are extensively used as various dielectrics for semiconductor industries. In general, silicon oxide cannot be used as resistance random access memory (RRAM) due to its insulating electrical properties. In this letter, we have successfully produced resistive switching and forming-free behaviors by zinc doped into silicon oxide. The current–voltage fitting data show that current transport mechanism is governed by Poole–Frenkel behavior in high-resistance state and Ohm's law in low-resistance state, consisting with filament theory. Additionally, good endurance and retention reliabilities are exhibited in the zinc-doped silicon oxide RRAM.**

***Index Terms*—Filament, resistive switch, silicon oxide, Zn.**

I. INTRODUCTION

RECENTLY, modern semiconductor nonvolatile memories (NVMs) have been scaled constantly to achieve large capacity while device features approach the sub-100-nm regime to store a large amount of information. Nevertheless, for conventional charge-storage-based memories [1]–[4], the increasing demand for device densities by scaling dimension is expected to be a major challenge due to the technical and physical limitations. Resistance random access memory (RRAM) is one of the promising candidates for next-generation NVMs, due to its simple cell structure, low operating voltage, high operating speed, and nondestructive readout [5]–[10].

For virgin RRAM devices [11], [12], an initial "forming" stage is needed to break down the resistance switching layer until, ultimately, devices present resistive switching behaviors. However, the voltage required for forming process can be relatively high, which not only imposes severe constraint from a circuit design perspective but also affects the endurance behavior of the memory device due to substantial trap generation during forming process. It is, therefore, necessary to develop an RRAM device that can be operated without "forming" process to enhance the performance metrics of the RRAM circuit.

Zinc element is a popular material applied to ZnO nanostructure [13] and IGZO TFT devices which can be used for flat-panel display [14]. Therefore, zinc metal doped into SiO_2 by cosputtering at room temperature was taken as the resistance switching layer of forming-free RRAM for the applications of system on panel. In addition, the conduction mechanism and material analyses were discussed to explain the influence of zinc metal doped in silicon oxide on forming-free resistive switching behaviors.

II. EXPERIMENTAL SETUP

First, a 30-nm $Zn:SiO_x$ thin film was deposited on a TiN/Ti/SiO_2/Si substrate by cosputtering with pure SiO_2 and Zn targets using an RF power of 200 W and a dc power of 10 W, respectively, in $Ar = 30$ sccm gas ambient with a working pressure of 4 mtorr. A Pt top electrode was deposited on the $Zn:SiO_x$ film to form Pt/$Zn:SiO_x/TiN$ sandwich structures. On the other hand, Pt/SiO_2/TiN sandwich structures were made by the same procedure as control samples. Finally, electrical device cells with a diameter of 4 μm were fabricated through lithography and lift-off techniques and measured by an Agilent B1500 semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows bipolar resistance switching characteristics of the Pt/$Zn:SiO_x/TiN$ device for dc voltage sweep operations. The current–voltage (I–V) properties of the sputtered SiO_2 layer cannot exhibit the RRAM properties due to its superior insulating properties shown in the lower right inset in Fig. 1(a). The voltage sweep bias was applied on the TiN electrode with the grounded Pt electrode shown in the lower left inset in Fig. 1(a). In particular, the device can exhibit resistive switching behavior without forming process, which is different to most of RRAM devices. In the initial state, the resistance state of

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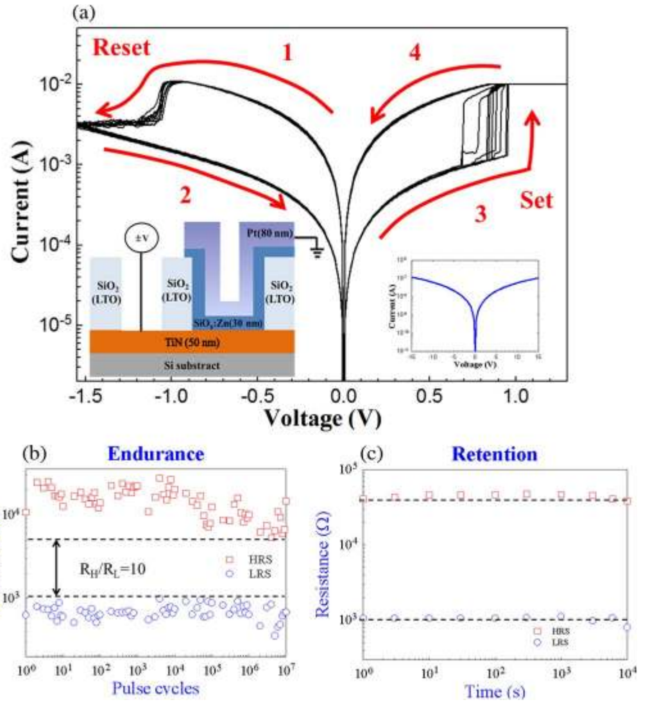

Fig. 1. (a) Bipolar resistance switching current–voltage (I–V) curves of the Pt/Zn : SiO_x/TiN device with compliance current of 10 mA. The bottom left inset shows the schematic diagram measured with grounded Pt electrode. The bottom right inset shows the I–V curve of the Pt/SiO_2/TiN device. (b) Endurance and (c) retention properties of Pt/Zn : SiO_x/TiN memory device. Read voltage was 0.1 V.

the Zn : SiO_x device was at low-resistance state (LRS). As the voltage was swept from 0 to -1.6 V without current compliance, an abrupt decrease in current was observed, where the cell switches to high-resistance state (HRS) from LRS, called as "reset process." In contrast, by sweeping the voltage from 0 to 1.3 V with a 10-mA current compliance, the resistance switched from HRS to LRS, called as "set process." Moreover, the programming current of the device can be complied by integrating a selecting transistor.

To further investigate the reliability properties of the NVM device, endurance and retention tests were evaluated in Fig. 1(b) and (c), respectively. For endurance tests, the HRS was switched to the LRS by applying a set voltage of 1.5 V for 10 ns, while the LRS was reset to the HRS by applying a reset voltage of -2 V for 15 ns. This resistive switching speed is competing with the operation speed of static random access memory. Both HRS and LRS resistance values were extracted at 0.1 V. The resistance ratio between the HRS and the LRS was about ten times and can be maintained during the 10^7 cycling bias pulse operations. The retention performance of the memory device was evaluated at 85 °C by measuring the resistance values of the LRS and HRS at 0.1 V with an interval. The resistance values of LRS and HRS remain almost constant even after 10^4 s. This implicates that the resistance state did not vary easily due to oxygen diffusion under retention test.

The HRS and the LRS of I–V curves were analyzed for the current conduction mechanisms to further discuss the resistance switching mechanisms in the Zn : SiO_x thin film (Fig. 2). The blue-square symbol in the I–V curve reveals that the current conduction in the HRS was dominated by the Poole–Frenkel conduction mechanism, followed by Ohm's law with the square root of the applied voltage at high fields (the lower right inset in Fig. 2). The ohmic conduction occurred at the green-triangle-marked region in the HRS due to intrinsic carrier in the silicon oxide (the lower left inset in Fig. 2). Moreover, the current conduction in the LRS complied with the ohmic conduction mechanism.

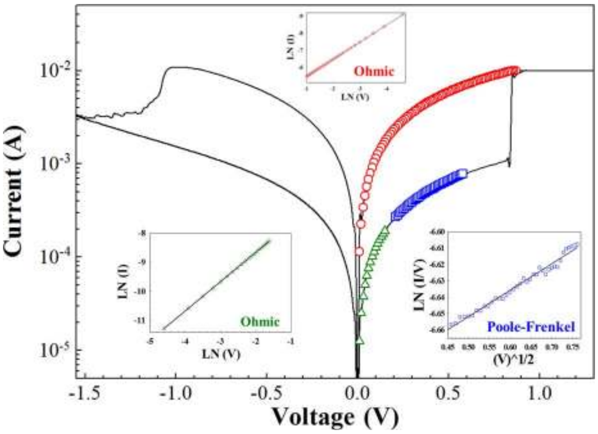

Fig. 2. I–V curve fitting of Pt/Zn : SiO_x/TiN memory device with various carrier transport mechanisms in different bias regions and resistance states.

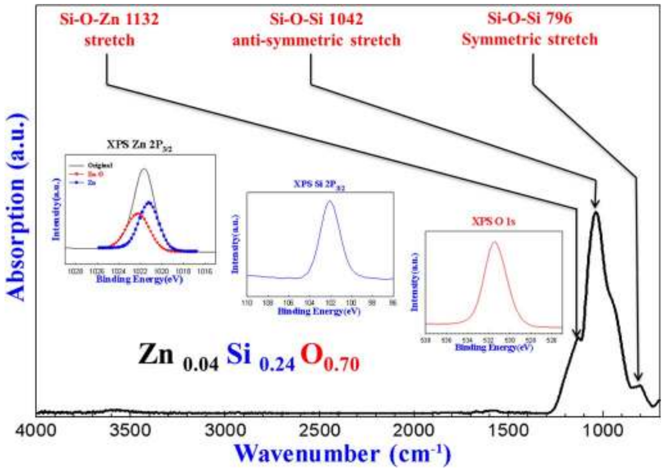

Fig. 3. FTIR spectra of Zn : SiO_x film measured in middle infrared region. The XPS spectra of Zn $2P_{3/2}$, Si $2P_{3/2}$, and O $1s$ core levels in Zn : SiO_x film are shown in the insets.

To analyze the influence of Zn doping on resistance switching characteristics in silicon oxide thin films, Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical bonding of the Zn : SiO_x film in this study. Fig. 3 shows that the Si–O–Zn stretch bonding was found in the Zn : SiO_x film at $1132\ \mathrm{cm}^{-1}$. In addition, the antisymmetric stretch mode and the symmetric stretch mode of Si–O–Si bonds were discovered at 1042 and $796\ \mathrm{cm}^{-1}$, respectively. According to these absorption peaks expressed in FTIR spectrums, we can confirm that the Zn element was bonded with the oxygen element in the silicon oxide film. To analyze the chemical composition of the Zn : SiO_x film in this study, X-ray photoelectron spectroscopy (XPS) of Zn $2P_{3/2}$, Si $2P_{3/2}$, and O $1s$ peaks was performed, and the XPS spectra are shown in the insets in Fig. 3. The mole fraction of Zn:Si:O in the Zn : SiO_x film was 4.9%:24.9%:70.2% calculated from the peak areas of Zn, Si, and O XPS spectra. In addition, compared with the areas of deconvolution peaks of Zn $2P_{3/2}$ core levels, we found that the mole fraction of

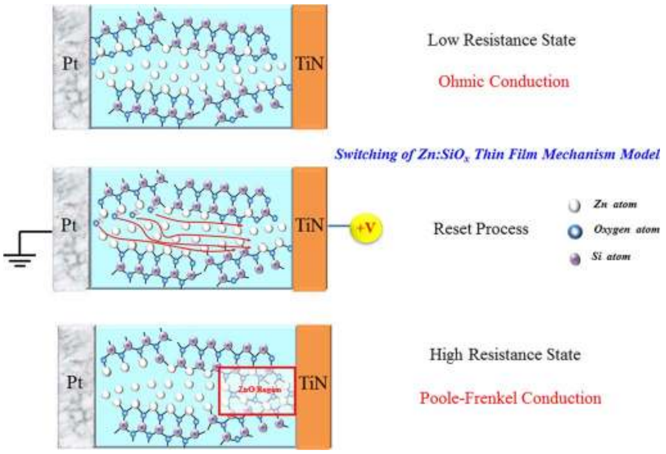

Fig. 4. Schematic diagram of reaction model in $\mathrm{Zn:SiO}_x$ film during resistive switching operation of the device.

ZnO:Zn was 45.1%:54.9% in the $\mathrm{Zn:SiO}_x$ film. The results of FTIR and XPS analyses demonstrated that the zinc metal is contained in the $\mathrm{Zn:SiO}_x$ film and the Si–O–Zn stretch bonding is formed on the boundary of zinc metal and silicon oxide.

Based on the electrical and material analyses, we propose a reaction model to explain the resistive switching behavior of Zn-doped silicon-oxide-based RRAM in Fig. 4. As the sample was fabricated to the $\mathrm{Pt/Zn:SiO}_x\mathrm{/TiN}$ device, the zinc element was wrapped by silicon oxide, leading to the zinc conductive filament connecting with the two electrodes. Therefore, the electrical current is dominated by ohmic conduction in LRS of the device. Then, the conductive current causes the negative oxygen ion surrounding the conductive filament close to the Pt electrode to drift to the TiN electrode, oxidizing the zinc element to zinc oxide (ZnO). Hence, the electrical current will be obstructed by the ZnO region shown in Fig. 4, which will make the electrical current transfer to HRS in the RRAM device. In virtue of the boundary of ZnO and silicon oxide existing strained bonds, the conduction mechanism in HRS of the device complied with the Poole–Frenkel conduction [15].

IV. CONCLUSION

In conclusion, the reproducible forming-free bipolar resistance switching characteristics have been achieved by doping Zn metal into silicon oxide film using cosputtering technique at room temperature. According to electrical and material analyses, the current transport mechanism of LRS in $\mathrm{Zn:SiO}_x$ RRAM was governed by ohmic conduction due to the conductive filament. Additionally, the current transport mechanism of HRS in $\mathrm{Zn:SiO}_x$ RRAM was governed by Poole–Frenkel conduction, which was attributed to the strained bonds at the boundary of ZnO and silicon oxide nearby the TiN electrode. Based on the reliability evaluation, the $\mathrm{Zn:SiO}_x$ RRAM satisfied the demand of modern NVMs.

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