Low Temperature Improvement Method on Zn:SiO$_x$ Resistive Random Access Memory Devices

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***Abstract*—To improve the resistive switching properties of the resistive random access memory (RRAM), the supercritical carbon dioxide ($SCCO_2$) fluid is used as a low temperature treatment. In this letter, the Zn:SiO$_x$ thin films are treated by $SCCO_2$ fluid mixed with pure water. After $SCCO_2$ fluid treatment, the resistive switching qualities of the Zn:SiO$_x$ thin films are carried out by XPS, fourier transform infrared spectroscopy, and IV measurement. We believe that the $SCCO_2$-treated Zn:SiO$_x$ thin film is a promising material for RRAM applications due to its compatibility with portable flat panel display.**

***Index Terms*—Nonvolatile memory, resistive switching, silicon oxide, zinc.**

I. INTRODUCTION

RECENTLY, the nonvolatile resistance random access memory (RRAM) has been widely discussed and investigated for applications in various memory devices because of its excellent memory characteristics, high storage capacity, long retention cycles, low operation voltage, and low electric consumption [1]–[6]. In addition, the various materials have been reported to possess resistive switching behaviors, silicon-based oxide is a promising material for RRAM applications because of its great compatibility in integrated circuit processes. Therefore, the research using silicon-based oxide as the resistance-switching layer was worthy of investigation. Lately, the liquid-like and excellent properties of the supercritical carbon dioxide ($SCCO_2$) fluid have attracted considerable research in efficiently transporting H_2O molecules and no damaging diffusion into the microstructures of dielectric layer at a low-temperature treatment. Decreased and passivated the traps and defects of thin films have their advantages [7]–[11]. In this letter, zinc metal doped into SiO_2 by co-sputtering at room temperature was taken as the resistance switching layer of RRAM. To demonstrate the resistive switching mechanism of zinc-doped SiO_2 (Zn:SiO$_x$) layer dominated by interface of TiN electrode or Zn:SiO$_x$ film, the Pt/Zn:SiO$_x$/TiN device was fabricated in virtue of inertia of Pt electrode as top electrode. In addition, the material and conduction mechanism analyses were discussed to explain the effect of the $SCCO_2$ fluid on Zn:SiO$_x$ resistive switching behaviors.

II. EXPERIMENTAL SETUP

The experimental samples were divided into two steps to verify the feasibility of $SCCO_2$ to improve the resistive switching properties of Zn:SiO$_x$ RRAM. First, the Zn:SiO$_x$ thin film (about 30 nm) was deposited on the TiN/Ti/SiO_2/Si substrate by co-sputtering with the pure SiO_2 and zinc targets. Sequentially, the Zn:SiO$_x$ thin films were placed in a supercritical fluid system with 165-ml chamber size at 150 °C for one hour, it was injected with 3000 psi $SCCO_2$ fluids, which were mixed with 0.5-ml pure H_2O. Therefore, the water will be solved into $SCCO_2$ fluids with a mole concentration of 0.17 M in the reactive chamber. Finally, the Pt top electrode of 200-nm thickness was deposited on Zn:SiO$_x$ film to form Pt/Zn:SiO$_x$/TiN sandwich structure. The entire electrical measurements of devices with the Pt electrode of 250-μm diameter were performed using Agilent B1500 semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

To analyze and discuss the influence of Zn element on resistance switching characteristics in SiO_2 thin film, the chemical bonding of the Zn:SiO$_x$ film was investigated by the

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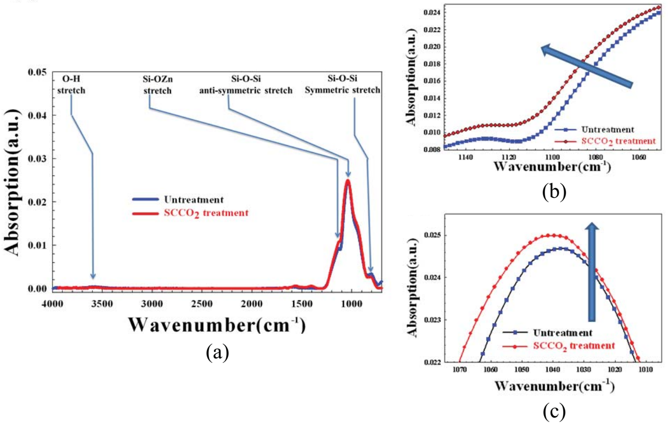


Fig. 1. (a) FTIR spectrums of Zn:SiO$_x$ film with (red line) and without (blue line) SCCO$_2$ treatment. (b) Enlargement of Si-O-Zn stretch bonding for SCCO$_2$-treated and untreated Zn:SiO$_x$. (c) Enlargement of the Si-O-Si bending mode bonds for SCCO$_2$-treated and untreated Zn:SiO$_x$.

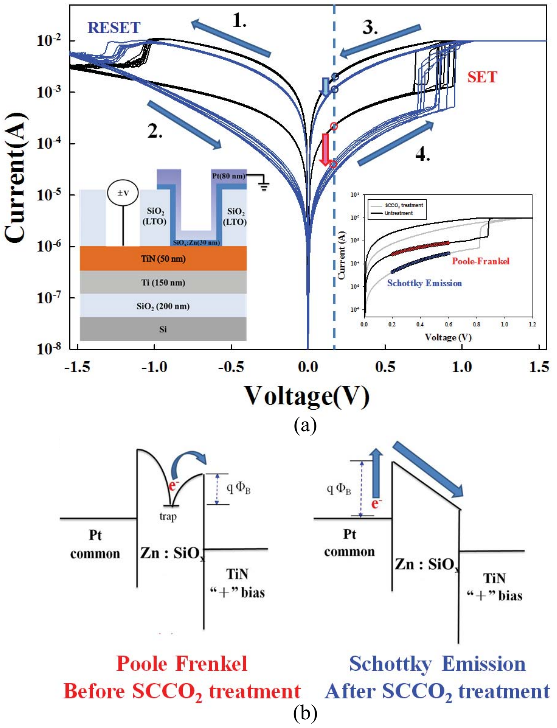


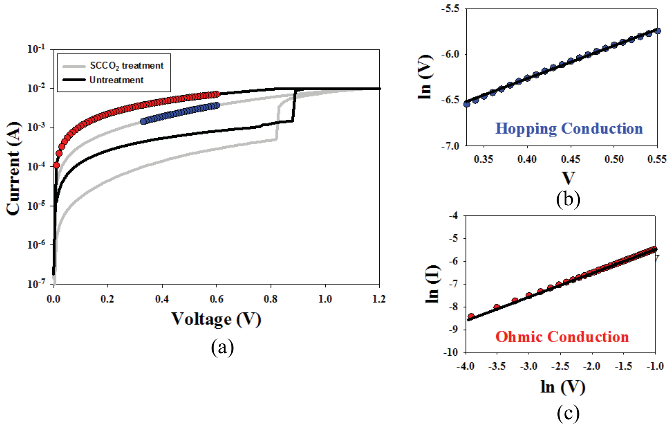
Fig. 2. (a) Current–voltage curves are the resistive switching characteristics of Zn:SiO$_x$ device with and without SCCO$_2$ treatment. The current conduction in HRS for Zn:SiO$_x$ device is transferred from Poole–Frenkel conduction to Schottky emission after SCCO$_2$ treatment. (b) Band diagrams of Zn:SiO$_x$ RRAM device before and after SCCO$_2$ treatment.

Fourier transform infrared spectroscopy (FTIR) in this letter. Fig. 1 shows the Si-O-Zn stretch bonding was found in the Zn:SiO$_x$ film at 1080 cm^{-1} from the FTIR spectrums. In addition, the anti-symmetric stretch mode and the symmetric stretch mode of Si-O-Si bonds were discovered at 1040 and 835 cm^{-1}, respectively. In addition, the peaks at 1080 cm^{-1} belonged to the Si-O-Zn stretch bonding and the peak at 1040 cm^{-1} belonged to the bending mode of Si-O-Si bonds were shown in Fig. 1(a) and (b). According to these absorption peaks expressed in FTIR spectrums, we can confirm the Zn element was bonded with oxygen element in the SiO$_2$ film. According to Beer's law, the Si-O-Zn stretch bonding intensity of the SCCO$_2$-treated thin films was improved from 0.018 to 0.02 shown in insert of Fig. 1(b). Besides, the Si-O-Si stretch bonding intensity of the SCCO$_2$ treated thin films was improved from 0.0247 to 0.0251 shown in Fig. 1(c). However, the intensity of O-H stretch bonding for SCCO$_2$-treated Zn:SiO$_x$ film was decreased. This result indicated that the oxygen and silicon atoms for the SCCO$_2$-treated Zn:SiO$_x$ film were combined and integrated and the Si-O-Si binding of thin films was closer and denser.

To analyze the influence of SCCO$_2$ treatment on chemical composition characteristics in Zn:SiO$_x$ thin film, the mole fraction of Zn:Si:O in the co-sputtered Zn:SiO$_x$ film was 4.9%:24.9%:70.2% by calculated from the peak areas of Zn, Si, and O XPS spectra. We also found that the Zn:Si:O in the SCCO$_2$-treated Zn:SiO$_x$ thin film was 3.8%:23.4%:72.08%. The intensity of Zn-O binding energy in Zn:SiO$_x$ thin film was increased from 45.13 to 64.7% based on the deconvolution signal from the Zn 2P$_{3/2}$ core level XPS spectra in Zn:SiO$_x$ film after SCCO$_2$ treatment. In addition, the mole fraction of oxygen in Zn:SiO$_x$ film was also increased from 70.2 to 72.08% after SCCO$_2$ treatment. This result indicated that operation current and resistance state of Zn:SiO$_x$ thin film were improved by SCCO$_2$ treatment process because of its oxidation and repaired damage ability.

In order to further discuss the resistance switching mechanisms in the co-sputtered and SCCO$_2$-treated Zn:SiO$_x$ thin film, the high resistive state (HRS) and the low resistive state (LRS) of current–voltage (I–V) curves were discussed and investigated for the current conduction mechanisms. Fig. 2(a) shows typical I–V characteristics of the Zn:SiO$_x$ RRAM devices with and without SCCO$_2$ treatment, which exhibit the bipolar behavior by applying bias on TiN electrode as shown in inset of Fig. 2(a) (left), and the current compliance was set at 10 mA to prevent the permanent breakdown of devices during operation. By sweeping the bias to negative over the reset voltage, a gradual decrease of current was presented to switch the cells from LRS to HRS (reset process). Conversely, the cell turns back to LRS while applying a larger positive bias than the set voltage (set process).

As shown in Fig. 2(a), the HRS state of the Zn:SiO$_x$ thin films treated by SCCO$_2$ was also decreased from 0.2 to 0.02 mA. The HRS state of the SCCO$_2$-treated films was ten times lower than untreated films. In applied voltage of 0.21∼0.58 V, the untreated thin films for HRS state were the Poole–Frankel emission conduction by ln(I/V)-V$^{1/2}$ curve fitting. According to experimental results, we suggested that doping zinc into SiO$_2$ resulted in an increased amount of hetero-defects in the Zn:SiO$_x$ thin films. For this reason, the electrons were transferred through the hetero-defects to make the current conduction dominated by Poole–Frenkel conduction. In addition, the SCCO$_2$-treated films for HRS state obey the Schottky Emission conduction in lnI-V$^{1/2}$ curve. The transfer of Poole–Frenkel to Schottky Emission conduction was attributed to defect and oxygen vacancy decreased and repaired in bulk Zn:SiO$_x$ thin films after SCCO$_2$ treatment [Fig. 2(b)].



(a) (b) (c)

Fig. 3. (a) Electrical characteristics of Zn:SiO$_x$ device with (blue cycle) and without (red cycle) SCCO$_2$ treatment. (b) A plot of ln(I) versus V in low resistance state (LRS) for SCCO$_2$-treated Zn:SiO$_x$ device. (c) A plot of ln(I) versus ln(V) in LRS for untreated Zn:SiO$_x$ device.

As shown in Fig. 3, the LRS state of the Zn:SiO$_x$ thin films prepared by SCCO$_2$ treatment was decreased from 2 to 0.8 mA at a reading voltage of 0.1 V. The LRS state of the SCCO$_2$-treated films was twice lower than untreated films. The untreated thin films exhibited the ohmic conduction by ln(I)-ln(V) curve fitting. This result indicated that the conductive filament formed by the current flowing through the zinc-induced defect in the Zn:SiO$_x$ film. In addition, the SCCO$_2$-treated thin films exhibited the hopping conduction by ln(I)-V curve fitting. According to the relationship of hopping conduction, $J = qNa\upsilon_0 e^{-qE_a/KT} e^{qaV/2dkT}$, where N, a, υ_0, E_a, and d are density of space charge, mean of hopping distance, intrinsic vibration frequency, barrier height of hopping, and film thickness, respectively. The hopping conduction is due to trapped electrons surpass to the E$_a$ barrier and form the leakage current for the SCCO$_2$-treated device. We found and suggested the active energy barrier lowering of SCCO$_2$-treated thin films caused by trapped electrons jump from the defects and form continuous potential well with positive charges [12]. The change of carrier transport in Zn:SiO$_x$ will reduce power consumption and joule heating degradation of RRAM due to hydration–dehydration reaction through SCCO$_2$ treatment at low temperature.

IV. CONCLUSION

In conclusion, the bipolar resistance switching characteristics were successfully achieved by doping Zn metal into SiO$_2$ film for untreated and treated SCCO$_2$ fluid treatment. To analyze HRS state of current fitting, the conduction mechanism of thin films for untreated and treated SCCO$_2$ process obeys the Poole–Frankel model and Schottky Emission model, respectively. For LRS state of current fitting, the untreated and treated thin films exhibited the ohmic contact model and hopping conduction model, respectively. Besides, we believed that the resistance switching performance of silicon oxide-based RRAM device can be improved in virtue of SCCO$_2$ low temperature treatment for IC applications. Finally, the smaller operated current and lower power consumption of the Zn:SiO$_x$ thin films can be effectively achieved by SCCO$_2$ treatment at low temperature for portable flat panel display applications.

REFERENCES

[1] T. M. Tsai, K. C. Chang, T. C. Chang, Y.-E. Syu, S.-L. Chuang, G.-W. Chang, G.-R. Liu, M.-C. Chen, H.-C. Huang, S.-K. Liu, Y.-H. Tai, D.-S. Gan, Y.-L. Yang, T.-F. Young, B.-H. Tseng, K.-H. Chen, M.-J. Tsai, C. Ye, H. Wang, and S. M. Sze, "Bipolar resistive RAM characteristics induced by nickel incorporated into silicon oxide dielectrics for IC applications," *IEEE Electron Device Lett.*, vol. 33, no. 12, pp. 1696–1698, Dec. 2012.

[2] Y. E. Syu, T. C. Chang, T. M. Tsai, Y. C. Hung, K. C. Chang, M. J. Tsai, M. J. Kao, and S. M. Sze, "Redox reaction switching mechanism in RRAM device with Pt/CoSiOX/TiN structure," *IEEE Electron Device Lett.*, vol. 32, no. 4, pp. 545–547, Apr. 2011.

[3] K. C. Chang, T. M. Tsai, T. C. Chang, Y. E. Syu, S. L. Chuang, C. H. Li, D. S. Gan, and S. M. Sze, "The effect of silicon oxide based RRAM with tin doping," *Electrochem. Solid-State Lett.*, vol. 15, no. 3, pp. H65–H68, 2012.

[4] Q. Liu, S. B. Long, W. Wang, Q. Y. Zuo, S. Zhang, J. N. Chen, and M. Liu, "Improvement of resistive switching properties in ZrO$_2$-based ReRAM with implanted Ti ions," *IEEE Electron Device Lett.*, vol. 30, no. 12, pp. 1335–1337, Dec. 2009.

[5] Y. Wang, Q. Liu, S. B. Long, W. Wang, Q. Wang, M. H. Zhang, S. Zhang, Y. T. Li, Q. Y. Zuo, J. H. Yang, and M. Liu, "Investigation of resistive switching in Cu-doped HfO$_2$ thin film for multilevel non-volatile memory applications," *Nanotechnology*, vol. 21, no. 4, p. 045202, 2010.

[6] Y. T. Li, S. B. Long, M. H. Zhang, Q. Liu, L. B. Shao, S. Zhang, Y. Wang, Q. Y. Zuo, and S. Liu, and M. Liu, "Resistive switching properties of Au/ZrO$_2$/Ag structure for low voltage nonvolatile memory applications," *IEEE Electron Device Lett.*, vol. 31, no. 2, pp. 117–119, Feb. 2010.

[7] C. T. Tsai, T. C. Chang, P. T. Liu, P. Y. Yang, Y. C. Kuo, K. T. Kin, P. L. Chang, and F. S. Huang, "Low-temperature method for enhancing sputter-deposited HfO$_2$ films with complete oxidization," *Appl. Phys. Lett.*, vol. 91, no. 1, pp. 012109-1–012109-3, Jul. 2007.

[8] T. M. Tsai, K. C. Chang, T. C. Chang, Y. E. Syu, K. H. Liao, B. H. Tseng, and S. M. Sze, "Dehydroxyl effect of Sn-doped silicon oxide resistance random access memory with supercritical CO$_2$ fluid treatment," *Appl. Phys. Lett.*, vol. 101, no. 11, pp. 112906-1–112906-4, Sep. 2012.

[9] M. C. Chen, T. C. Chang, S. Y. Huang, K. C. Chang, H. W. Li, S. C. Chen, J. Lu, and Y. Shi, "A low-temperature method for improving the performance of sputter-deposited ZnO thin-film-transistors with supercritical fluid," *Appl. Phys. Lett.*, vol. 94, no. 16, pp. 162111-1–162111-3, Apr. 2009.

[10] K. C. Chang, T. M. Tsai, T. C. Chang, Y. E. Syu, C.-C. Wang, S. K. Liu, S. L. Chuang, C. H. Li, D. S. Gan, and S. M. Sze, "Reducing operation current of Ni-doped silicon oxide resistance random access memory by supercritical CO$_2$ fluid treatment," *Appl. Phys. Lett.*, vol. 99, no. 26, pp. 263501-1-263501-4, Dec. 2011.

[11] T. M. Tsai, K. C. Chang, T. C. Chang et al., "Origin of hopping conduction in Sn-doped silicon oxide RRAM with supercritical CO$_2$ fluid treatment," *IEEE Electron Device Lett.*, vol. 33, no. 12, pp. 1693–1695, Dec. 2012.

[12] T. Y. Tseng and H. Nalwa, *Handbook of Nanoceramics and Their Nased Nano Devices*, Valencia, CA, USA: American Scientific Pub., 2009, pp. 175–176.