Hopping Effect of Hydrogen-Doped Silicon Oxide Insert RRAM by Supercritical CO_2 Fluid Treatment

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***Abstract*—In this letter, we introduced hydrogen ions into titanium metal doped into SiO_2 thin film as the insulator of resistive random access memory (RRAM) by supercritical carbon dioxide $(SCCO)_2$ fluid treatment. After treatment, low resistance state split in to two states, we find the insert RRAM, which means it has an operating polarity opposite from normal RRAM. The difference of the insert RRAM is owing to the resistive switching dominated by hydrogen ions, dissociated from OH bond, which was not by oxygen ions as usual. The current conduction mechanism of insert RRAM was hopping conduction due to the metal titanium reduction reaction through $SCCO_2$.**

***Index Terms*—Hopping conduction, resistive random access memory (RRAM), supercritical fluid.**

I. INTRODUCTION

RECENTLY, next-generation memories have been widely investigated. Resistance random access memory (RRAM) is one of the most popular memory devices, due to its simple structure, high-switching speed, low-operation power, and nonvolatile characteristic [1]–[8]. Besides, silicon-based oxide is a promising material for RRAM application owing to its great compatibility in IC processes. Thus, the silicon-base oxide was selected as the resistance-switching layer in our research. The supercritical carbon dioxide ($SCCO_2$) fluid mixed with pure water as co-solvent treating thin film has been regarded as an efficient way to transport H_2O molecules into the microstructure of the switching layer to improve dielectric properties, because of its high penetration and liquid-like characteristics [9]–[11]. In this research, titanium metal doped into SiO_2 ($Ti:SiO_2$) by co-sputtering at room temperature was taken as the resistance switching layer of RRAM. The conduction mechanism and material analyses were discussed to explain the phenomenon of insert RRAM occurred after $SCCO_2$ fluid treatment.

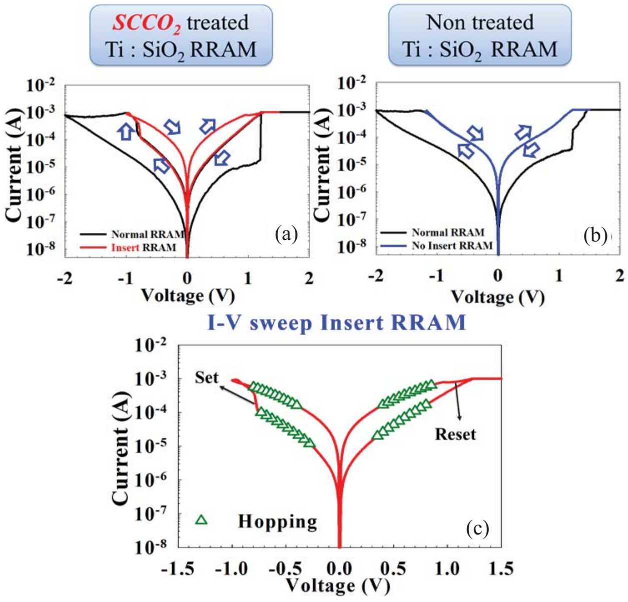

Fig. 1. (a) Current–voltage curve of the resistive switching characteristic of $Ti:SiO_2$ device with $SCCO_2$ treatment. (b) Current–voltage curve of the resistive switching characteristic of $Ti:SiO_2$ device without $SCCO_2$ treatment. (c) Current conduction curve of the insert RRAM. The conduction mechanism is the hopping conduction both at HRS and LRS.

II. EXPERIMENTAL SETUP

First, the $Ti:SiO_2$ thin film (about 10 nm) was deposited on the $TiN/Ti/SiO_2/Si$ substrate by co-sputtering with the pure SiO_2 and titanium targets. After that, the $Ti:SiO_2$ thin films were put into the chamber of supercritical fluid system at 120 °C for 1 h, the chamber was injected with $SCCO_2$ fluid at the pressure of 3,000 psi which were mixed with 5 vol%

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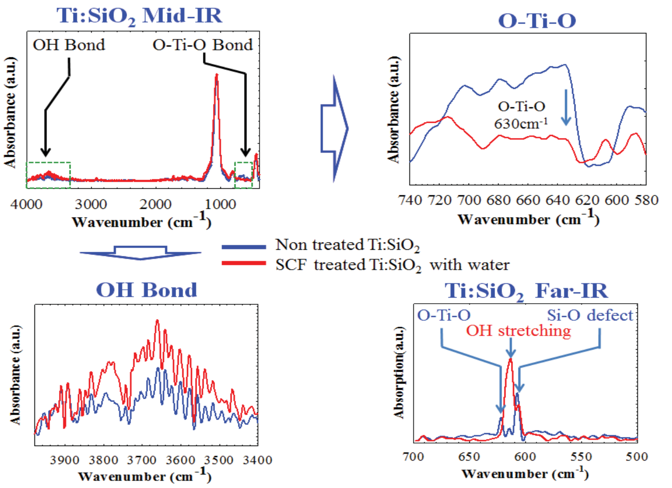

Fig. 2. FTIR spectrums of Ti:SiO$_2$ film with and without SCCO$_2$ treatment. The signal of O–H and O–H stretching bond increased, and the O–Ti–O bond decreased after SCCO$_2$ treatment.

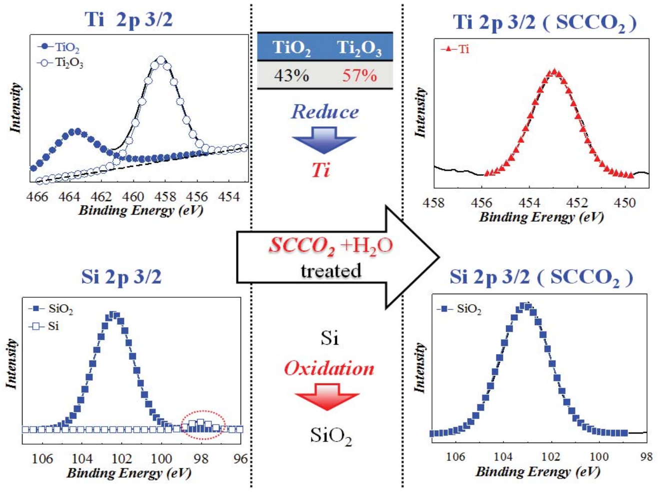

Fig. 3. XPS spectra of Ti 2p$_{3/2}$ and Si 2p$_{3/2}$ core level in Ti:SiO$_2$ film before and after SCCO$_2$ treatment. By quantum analysis, The mole fraction of O–Ti–O bonds in Ti:SiO$_2$ film is reduced obviously but that of O–Si–O bonds are increased after SCCO$_2$ treatment.

pure H_2O. Finally, the Pt top electrode of 200 nm thickness was deposited on Ti:SiO$_2$ film to form the RRAM devices with Pt/Ti:SiO$_2$/TiN structure. The electrical analyses of all devices were performed using Agilent B1500 semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

In order to understand the influence of SCCO$_2$-treated Ti:SiO$_2$ RRAM device, the device was measured for electrical analyses before and after SCCO$_2$ fluid treatment. The insert RRAM appeared after the SCCO$_2$ treatment shown as Fig. 1(a), which is opposite to normal RRAM in operating polarity. In the insert RRAM, the set process was completed in the negative bias sweep cycle. In contrast, the reset process was accomplished in the positive bias sweep cycle. However, the insert RRAM was not found in the Ti:SiO$_2$ RRAM device before SCCO$_2$ treatment shown as Fig. 1(b).

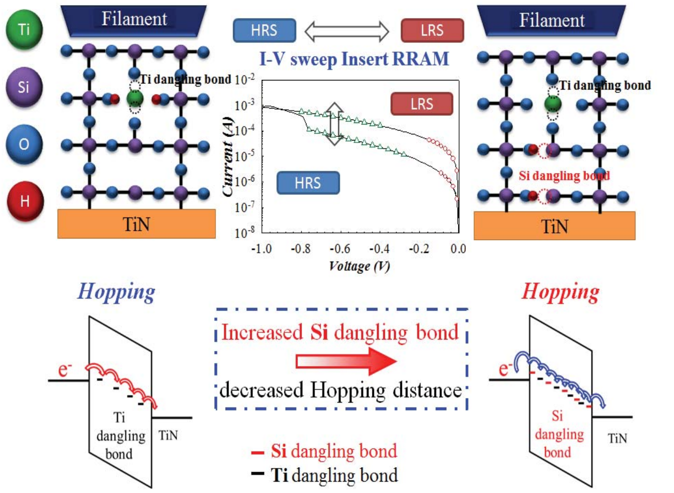

Fig. 4. Diagram of the resistive switching of the insert RRAM, and the energy band of carrier hopping effect in the resistance-switching layer.

The HRS of insert RRAM and the low resistance state (LRS) of normal RRAM have same state. In order to present the insert RRAM, we have to control the stop voltage precisely so as to get sweep cycles to analyze its characteristics. Besides, the current conduction mechanism was dominated by hopping conduction both in HRS and LRS of the insert RRAM shown as Fig. 1(c). And the hopping conduction equation is $J = qNa\upsilon_0 e^{-q\phi_T/kT} e^{qaV/2dkT}$, where N, a, ϕ_T, υ_0, and d are density of space charge, mean of hopping distance, barrier height of hopping, intrinsic vibration frequency, and film thickness, respectively. To investigate the interesting phenomena on resistive switching of insert RRAM, the Fourier transform infrared spectroscopy (FTIR) was conducted to do material analyses. In the Fig. 2, the signal of O–Ti–O bond at 630 cm^{-1} was decayed after SCCO$_2$ fluid treatment, and the signal of OH bond at 3400–3600 cm^{-1} was increased. Meanwhile, the signal of O–H stretching bond at 636 cm^{-1} was also increased after SCCO$_2$ fluid treatment [12], which can be observed in Far-IR region of FTIR. According to Beer's law, the absorption coefficient and the thickness of the film did not change during the SCCO$_2$ fluid treatment, the intensity of signal is proportional to the concentration of the corresponding bond. Therefore, the TiO$_2$ was deoxidized to Ti element and Si was oxidized in the Ti:SiO$_2$ film after SCCO$_2$ fluid treatment. Besides, the OH bond was brought into the film through treatment. Then, the material analyses were used to verify the change of oxidation number of Ti and Si by X-ray photoelectron spectroscopy (XPS) shown in Fig. 3. Before SCCO$_2$ fluid treatment, there was 43% of TiO$_2$ and 57% of Ti$_2$O$_3$ in the titanium oxide of Ti:SiO$_2$ film, but no metal titanium exist in the film. Based on the deconvolution of Si 2P$_{3/2}$ core level, a few Si bonding signal was found in Ti:SiO$_2$ film. After the SCCO$_2$ treatment, the titanium oxide of Ti:SiO$_2$ film was deoxidized and changed into metal titanium while silicon of Ti:SiO$_2$ film was oxidized into silicon oxide. According to material analyses, we found OH bond increased and some oxidation–reduction reactions happened in Ti:SiO$_2$ film during SCCO$_2$ fluid treatment. So, we proposed a model to explain the electrical phenomenon of insert RRAM shown in Fig. 4. The nucleus of metal titanium caused the defect of the film, leading to the hopping conduction at HRS of insert RRAM. Owing to the increasing of OH bond, the hydrogen ions generated from OH bond broken were attracted to TiN electrode when supplied a negative bias, resulting in Si–O bond broke during the hydrogen ions migration. The silicon dangling bond also increased the density of defect to reduce the hopping distance, leading to the increase of current in $SCCO_2$-treated device. This would make the set process occur at a negative bias. On the contrary, the reset process of insert RRAM would occur at positive bias due to the opposite migration of hydrogen ions.

IV. CONCLUSION

In conclusion, the insert RRAM which is opposite to normal RRAM in operating polarity was observed in the $Ti:SiO_2$ device after $SCCO_2$ fluid treatment. According to material analyses of XPS and FTIR, we found the $Ti:SiO_2$ film could increase OH bond through $SCCO_2$ treatment. The OH bond provided plenty of hydrogen ions during negative bias, leading to set process. The dangling bond from nucleus of metal titanium and Si–O broken bond supplied more defect to resulting carrier hopping conduction by means of the hydrogen ions migration. These phenomena will result in insert RRAM for $SCCO_2$-treated $Ti:SiO_2$ RRAM.

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