Improvement mechanism of resistance random access memory with supercritical CO2 fluid treatment

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\textbf{A B S T R A C T}
We demonstrated that the supercritical CO2 fluid treatment was a new concept to efficiently reduce the operation current of resistance random access memory. The dangling bonds of tin-doped silicon oxide (Sn:SIO) thin film were passivated by the hydration–dehydration reaction through supercritical CO2 fluid treatment, which was verified by the XPS and FTIR analyses. The current conduction mechanism of low resistance state in post-treated Sn:SIO thin film was transferred to hopping conduction from Ohmic conduction. Furthermore, the current conduction mechanism of high resistance state in the memory device was transferred to Schottky emission from Frenkel–Poole conduction. The phenomena were attributed to the discontinuous metal filament formed by hydration–dehydration reaction in Sn:SIO thin film through supercritical fluid treatment. Finally, a reaction model was proposed to explain the mechanism of current reduction in Sn:SIO thin film with supercritical CO2 fluid treatment.

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\section{1. Introduction}
For the increasing demands for portable electronic products, nonvolatile memory has been widely applied as information storage device due to its low power consumption properties. Modern semiconductor nonvolatile memories are scaled constantly to achieve large capacity while device features approach the sub-100-nm regime. However, the increasing demand for device densities by scaling dimension is expected to be a major challenge due to the technical and physical limitation. To surmount the technical and physical limitation issues of conventional charge storage-based memories [1–8], the resistance random access memory (RRAM) constructed of an insulating layer sandwiched by two electrodes is widely investigated by industries and academics. The RRAM is a great potential candidate for next-generation nonvolatile memory due to their superior characteristics such as lesser cost, simple structure, high-speed operation, and non-destructive readout [9,10]. Various materials have been reported to possess resistive switching behaviors, such as solid-electrolyte-based RRAM [11,12], transition metal oxides (MnO\textsubscript{2}, ZrO\textsubscript{2}, HfO\textsubscript{x}) [13–15,9,16,17], and organic material [18]. In addition, many switching mechanisms of RRAM have been proposed to explain resistive switching phenomenon, such as conductive filament formation [19], valence change [20], and Schottky barrier [21]. However, the underlying mechanism of resistive switching behavior is still not yet understood clearly. Silicon-based oxide is a promising material for RRAM applications because of its great compatibility in integrated circuit (IC) process.

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Therefore, the research using silicon-based oxide as the resistance-switching layer was worthy of investigation.

In our preceding research, supercritical CO₂ (SCCO₂) fluid technology was used to improve the dielectric properties and performance of various thin film transistors (TFTs), such as hydrogenated amorphous-silicon TFTs and ZnO TFTs [22–30]. Supercritical phase is peculiar with its characteristics of high penetration of gas and solubility of liquid. The supercritical water fluid has tremendous oxidation property [31]. However, high critical temperature and high critical pressure are essential condition to achieve supercritical water fluid, which is difficult to realize through modern facilities. By adding a little water into supercritical CO₂ fluids, the liquid water can attain to the supercritical fluid phase due to the phase close to idea solution.

In this work, tin metal doped into silicon oxide by co-sputtering at room temperature was taken as the resistance switching layer of RRAM. To evaluate the resistive switching properties of tin-doped silicon oxide (Sn:SiOₓ) layer, the Pt/Sn:SiOₓ/TiN device was fabricated at clean room. Moreover, the material and conduction mechanism analyses were executed to explain the influence of Sn metal doped in silicon oxide on resistive switching behaviors. In addition, the Pt/SCCO₂-treated Sn:SiOₓ/TiN sandwiched devices were fabricated to investigate the effect of SCCO₂ on resistive switching properties of Sn:SiOₓ thin film. The effects of SCCO₂ treatment on resistive switching behaviors of Sn:SiOₓ thin film was also evaluated by material and carrier conduction mechanism analyses. Furthermore, the reaction mechanism in RRAM with SCCO₂ fluid was also discussed to explain the reason of electrical property improvement on Sn:SiOₓ RRAM.

2. Experimental

The experimental specimens were prepared as follows: In the first group, the Sn:SiOₓ thin film (about 30 nm) was deposited on the TiN/Ti/SiO₂/Si substrate by co-sputtering with the pure SiO₂ and Sn targets. The sputtering power was fixed at RF power 200 W and 3 W for SiO₂ and Sn targets respectively. The co-sputtering was executed in argon ambient (Ar = 30 sccm) with a working pressure of 0.789 Pa at room temperature. In the second group, the Sn:SiOₓ thin films were put into the reactive chamber of supercritical fluid system, and then the SCCO₂ fluid mixed with 0.5 ml water were syringed into the reactive chamber to treat the specimens. The passivation efficiency increases with the rising temperature and CO₂ pressure as long as exceeding the critical point, which are 31 °C with 7.3 MPa CO₂. But owing to the limitation of our experiment equipment, the water-mixed supercritical CO₂ fluids were heated and pressured to 120 °C and 20.4 MPa in the stainless steel chamber of supercritical fluid system for 1 h. Finally, the Pt top electrode of 200 nm thickness was deposited on Sn:SiOₓ thin film to form electrical devices with Pt/Sn:SiOₓ/TiN sandwich structures by DC magnetron sputtering. By contrast, the Pt/SiO₂/TiN sandwich structures were made by same process procedure with a sputtered SiO₂ layer instead of a Sn:SiOₓ layer as control samples. The entire electrical measurements of devices with the Pt electrode of 250 μm diameter were performed using Agilent B1500 semiconductor parameter analyzer. Besides, the Fourier transform infrared spectroscopy (FTIR) measured by Bruker VERTEX 70v spectrometer in far infrared region and X-ray photoelectron spectroscopy (XPS) were used to analyze the chemical composition and bonding of these insulator materials, respectively.

3. Results and discussion

The “forming process” is required to activate all of the Sn:SiOₓ RRAM devices, using dc voltage sweeping with a compliance current of 2 mA. The leakage current of the Sn:SiOₓ RRAM devices after SCCO₂ treatment was lower than that of pre-treatment devices (Fig. 1). This phenomenon is attributed to the improvement on dielectric properties through SCCO₂ treatment, which has been reported by our previous study [23]. The voltage sweep bias was applied on TiN electrode with the grounded Pt electrode as shown in the bottom left inset of Fig. 2. After the forming process, a gradual decrease in current was observed where the cell switches from low resistance state (LRS) to high resistance state (HRS), called as “reset process”, by sweeping the voltage from 0 to −1.8 V without current compliance. On contrast, as the voltage was swept from 0 to 1.2 V with a 5 mA current compliance, the resistance switched from HRS to LRS, called as “set process”. In the Pt/Sn:SiOₓ/TiN device, the resistance ratio of HRS and LRS is about 10² times at a reading voltage of 0.1 V. The electrical current-voltage properties of the Sn:SiOₓ devices were compared before and after SCCO₂ treatment (Fig. 2). The current of Sn:SiOₓ devices is reduced at 0.1 V reading voltage after SCCO₂ treatment. To investigate the interesting phenomena, we analyzed the current conduction mechanism of Sn:SiOₓ thin film with and without SCCO₂ treatment as shown in Fig. 3. The carrier transport in LRS state of Sn:SiOₓ device was dominated by Ohmic conduction in the Sn:SiOₓ layer. After SCCO₂ treatment, the current conduction mechanism will transfer to hopping conduction because of the change of material properties. In addition, we also analyzed the current conduction mechanism in HRS of Sn:SiOₓ with and without SCCO₂ treatment as shown in Fig. 4. The relationship in the curve of ln(I/V) versus the square root of voltage (Fig. 4).
**Fig. 3.** The current conduction curves in the LRS of Sn:SiO\textsubscript{x} devices before and after SCCO\textsubscript{2} treatment. The current vs. voltage diagrams were measured at different temperature environments in the Sn:SiO\textsubscript{x} film before and after SCCO\textsubscript{2} treatment.

**Fig. 4.** The current conduction curves in the HRS of Sn:SiO\textsubscript{x} devices before and after SCCO\textsubscript{2} treatment. The fitting of current vs. voltage curves in the HRS of the devices before and after SCCO\textsubscript{2} treatment was drawn in right side.
of the applied voltage ($V^{1/2}$) is linear. According to the relationship of Frenkel–Poole conduction, $I \propto V \exp[(q/kT)(2a\sqrt{V} - \phi_B)]$, where $a$ is $\sqrt{q/4\pi e d}$, $\phi_B$ is the trap barrier height, and $d$ is the insulator thickness. The Frenkel–Poole conduction is due to emission of trapped electrons into conduction band. The supply of electrons from the traps is through thermal excitation. The barrier reduction is larger than in the case of Schottky emission by a factor of 2, which can be obtained as compared with the slope of the plot of $\ln(I)$ versus $V^{1/2}$ based on the formula of Schottky emission, $I \propto I^2 \exp[(q/kT)(a\sqrt{V} - \phi_B)]$, where $\phi_B$ is the Schottky barrier height. The results revealed that the carrier transport of Sn:SiO$_2$ film was dominated by Frenkel–Poole conduction due to the trap in the film. After SCCO$_2$ treatment, the current conduction mechanism will transfer to Schottky emission because of the improvement of dielectric properties. Therefore, we utilized the material spectra analyses to find out the reason of different electrical transfer mechanisms in conduction current before and after SCCO$_2$ treatment. Compared the FTIR spectra of Sn:SiO$_2$ film with and without SCCO$_2$ treatment (Fig. 5), we found that the absorption peak of Sn–O bond at 586 cm$^{-1}$ was increased after SCCO$_2$ treatment. The result implies that the density of Sn–O bond was increased in the Sn:SiO$_2$ film after SCCO$_2$ treatment. In addition, the absorption of Si-O-Si stretch bond at 450 cm$^{-1}$ was also increased after SCCO$_2$ treatment, illustrating the content of silicon oxide bonding in the film also increased [32,33]. To analyze the chemical composition of Sn:SiO$_2$ film in this study, X-ray photoelectron spectroscopy (XPS) of Sn 3d$_{5/2}$, Si 2p and O 1s peaks were performed. After compared with the peak area of Sn, Si and O XPS spectra, the mole fraction of Sn: Si: O in the co-sputtered Sn:SiO$_2$ film was 0.3%: 29.5%: 70.2%. According to XPS spectra analyses for Sn 3d$_{5/2}$ core level (Fig. 6), the mole fraction of Sn–O bond was obviously risen but that of Sn element was decreased in Sn:SiO$_2$ film after SCCO$_2$ treatment. Besides, the mole fraction of Si–O bond was substantially increased in contrast with that of Si–OH bond after SCCO$_2$ treatment in terms of the XPS spectra analyses of Si 2p core level as shown in Fig. 6. Table 1 shows the comparison of the areas of deconvolution peaks of Sn 3d$_{5/2}$ and Si 2p core levels. We found the mole fraction (SnO$_2$:Sn = 50.6%:49.4%) in Sn:SiO$_2$ film is changed to that (SnO$_2$:Sn = 70.6%:29.4%) after SCCO$_2$ treatment. Also, the mole fraction (SiOH:SiO$_2$ = 18.9%:81.1%) in Sn:SiO$_2$ film is changed to that (SiOH:SiO$_2$ = 66.4%:33.6%) in the post-treated Sn:SiO$_2$ film. Therefore, we infer that the level of oxidation would increase and
accompanied with dehydration in the post-treated film. These results were consistent with the above-mentioned FTIR analyses.

Based on the electrical and material analyses, we proposed a reaction mode to explain reaction mechanism of Sn:SiO film with SCCO$_2$ treatment as shown in Fig. 7. As the sample was put into the water-mixed SCCO$_2$ fluid environment, the H$_2$O molecule was carried into the grain boundary of Sn:SiO film by SCCO$_2$ fluid, which is attributed to the high penetration ability of SCCO$_2$ fluid. As the H$_2$O molecule approached to grain boundary of the film, the dehydration reaction occurred in the Sn:SiO film. Then, monomolecular CO$_2$ in supercritical fluids induces the dehydration of neighbor hydroxyl groups so as to form Si–O–Si and Sn–O–Si network-like bonding in the film. The mechanism is called hydration–dehydration reaction of SCCO$_2$ fluids in Sn:SiO film. As for the LRS of Sn:SiO film, the conductive filament will be formed in pre-treated Sn:SiO film after the forming process. The conductive filament will be connected with dangling bond in the switching region of the film. The carriers were transported through these dangling bonds, leading to the current conduction dominated by Ohmic conduction. If the Sn:SiO film was put into the SCCO$_2$ fluid environment, the H$_2$O molecule was carried into the grain boundary of the film by SCCO$_2$ fluid, which is attributed to the high penetration ability of SCCO$_2$ fluid. Hence, the tin metal in Sn:SiO thin film will be isolated due to hydration–dehydration reaction by SCCO$_2$ treatment. Only if the conductive filament formed in the Sn:SiO film, the carrier will hop through the isolated tin metal in the switching region of the post-treated film. This phenomena will make the electrical current conduction in LRS of Sn:SiO film transferred from Ohmic conduction to hopping conduction as shown in Fig. 8. Owing to the trap of Sn:SiO film can be passivated by SCCO$_2$ treatment, the electrical current conduction in HRS of Sn:SiO film will be transferred to Schottky emission from Frenkel–Poole conduction as shown in Fig. 9. This phenomenon will cause the improvement of dielectric properties of thin film, leading to decrease the operation current and the power consumption of RRAM.

**Mechanism Model**

**Table 1**
Comparison of the areas of deconvolution peaks of Sn 3d$_{5/2}$ and Si 2p core levels before and after SCCO$_2$ treatment.

<table>
<thead>
<tr>
<th></th>
<th>SnO$_2$</th>
<th>Sn</th>
<th>SiOH</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before SCCO$_2$</td>
<td>50.6%</td>
<td>49.4%</td>
<td>66.4%</td>
<td>33.6%</td>
</tr>
<tr>
<td>After SCCO$_2$</td>
<td>70.6%↑</td>
<td>29.4%↓</td>
<td>18.9%↓</td>
<td>81.1%↑</td>
</tr>
</tbody>
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Fig. 7. The schematic diagram of hydration–dehydration reaction mechanism on Sn:SiO film to illustrate defect passivation through SCCO$_2$ treatment.

**Mechanism Model at LRS**

**Before SCCO$_2$: Ohmic Conduction**

**After SCCO$_2$: Hopping Conduction**

Fig. 8. The schematic diagram of carrier hopping model in Sn:SiO film after SCCO$_2$ treatment.
4. Conclusion

In summary, the operation current of Sn-doped silicon oxide RRAM device was reduced by supercritical fluid treatment in this study. The water molecular can be brought into the film to passivate the dangling bond of grain boundary in resistive switching layer by supercritical CO$_2$ fluid. In virtue of the phenomena, the discontinuous conductive filament in Sn:SiO$_2$ film was formed by hydration–dehydration reaction through SCCO$_2$ fluids. The operation current of RRAM can be reduced due to the decrease of defect in the layer, which results in low power consumption. Besides, the effect of Joule heating can also be improved for the device. Therefore, supercritical fluid treatment can enhance the properties of resistive switching layer of RRAM device. We believe that the technology is beneficial to the development of RRAM for the next generation nonvolatile applications.

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