Origin of Hopping Conduction in Sn-Doped Silicon Oxide RRAM With Supercritical CO_2 Fluid Treatment

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***Abstract*—In this letter, we investigate the origin of hopping conduction in the low-resistance state (LRS) of a resistive random access memory device with supercritical CO_2 fluid treatment. The dangling bonds of a tin-doped silicon oxide ($Sn:SiO_x$) thin film were cross linked by the hydration–dehydration reaction through supercritical fluid technology. The current conduction mechanism of the LRS in the posttreated $Sn:SiO_x$ thin film was transferred to hopping conduction from Ohmic conduction, owing to isolation of metal tin in the $Sn:SiO_x$ thin film by hydration–dehydration reaction. The phenomena can be verified by our proposed reaction model, which is speculated by the X-ray photoelectron spectroscopy analyses.**

***Index Terms*—Hopping conduction, hydration–dehydration reaction, resistance random access memory (RRAM), supercritical fluid.**

I. Introduction

TO SURMOUNT the technical and physical limitation issues of conventional charge storage-based memory devices [1]–[5], the resistance random access memory (RRAM) device is constructed of an insulating layer sandwiched by two electrodes. This is a great potential candidate for the next-generation nonvolatile memory due to their superior characteristics such as lesser cost, simple structure, high-speed operation, and nondestructive readout [6], [7].

In our previous research, supercritical CO_2 ($SCCO_2$) fluid technology was used to improve the dielectric properties and performance of various thin-film transistors (TFTs), e.g., hydrogenated amorphous-silicon TFTs and ZnO TFTs [8]–[15]. Supercritical phase is peculiar with its characteristics of high penetration of gas and solubility of liquid. The property of supercritical water fluid has tremendous oxidation [16]. However, high critical temperature and high critical pressure are essential condition to lead to supercritical water fluid, which is difficult to achieve through modern facilities. By adding a little water into supercritical CO_2 fluids, the liquid water can achieve the phase of supercritical fluids due to the phase close to the idea solution.

The material of Sn-doped silicon oxide ($Sn:SiO_x$) used as a resistive switching layer has been studied in our previous work [17]. Therefore, the $Pt/Sn:SiO_x/TiN$ sandwiched devices were fabricated to investigate the effect of $SCCO_2$ on resistive switching properties of $Sn:SiO_x$ thin films. The effects of $SCCO_2$ treatment on resistive switching behaviors of $Sn:SiO_x$ thin films were evaluated by material and carrier conduction mechanism analyses. Because the supercritical fluid has gaslike and high-pressure properties to effectively diffuse into nanoscale without damage [18], the dangling bonds of $Sn:SiO_x$ thin films were cross linked by the hydration–dehydration reaction.

II. Experimental Setup

The experimental specimens were prepared as follows: the $Sn:SiO_x$ thin film (about 30 nm) was deposited on the $TiN/Ti/SiO_2/Si$ substrate by cosputtering with the pure SiO_2 and Sn targets. The sputtering power was fixed at RF power of 200 and 3 W for SiO_2 and Sn targets, respectively. The cosputtering was executed in argon ambient ($Ar = 30$ sccm) with a working pressure of 6 mTorr at room temperature. In contrast, the $Sn:SiO_x$ thin films were put into the supercritical fluid system with 165-mL chamber size, and then, the $SCCO_2$ fluid mixed with 0.5-mL water were syringed into the reactive chamber to treat the specimens. Therefore, the water will be solved into $SCCO_2$ fluids with a mole concentration of 0.17 M in the reactive chamber. During the treatment, the water-mixed supercritical CO_2 fluids were heated and pressured to 120 °C and 3000 lbf/in2, respectively, in the stainless steel chamber of the supercritical fluid system for 1 h. Ultimately, the Pt top electrode with a thickness of 200 nm was deposited on the $Sn:SiO_x$ thin film to form electrical devices with

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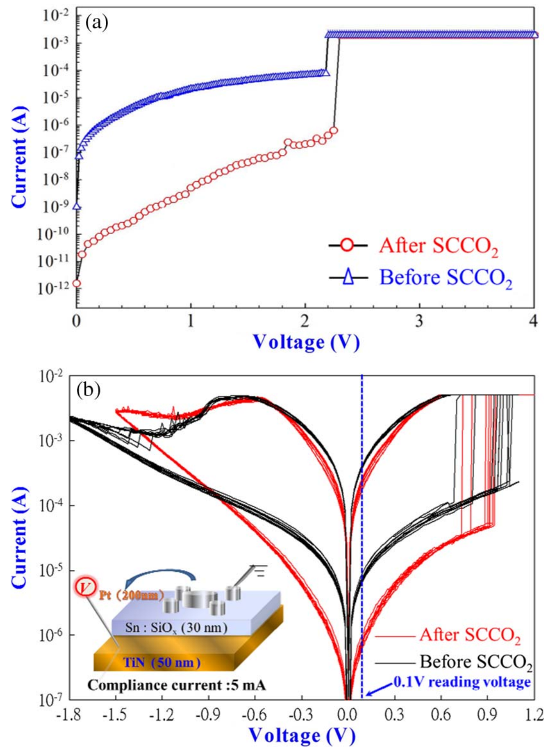

Fig. 1. (a) Forming current curves of the Sn:SiO$_x$ RRAM devices before and after SCCO$_2$ treatment. (b) Black and red curves are the resistive switching characteristics of the Sn:SiO$_x$ film before and after SCCO$_2$ treatment, respectively. The current of the posttreated Sn:SiO$_x$ film is reduced.

Pt/Sn : SiO$_x$/TiN sandwich structures by dc magnetron sputtering. The entire electrical measurements of devices with the Pt electrode of 250-μm diameter were performed using Agilent B1500 semiconductor parameter analyzer. In addition, X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition and bonding of these insulator materials, respectively.

III. Results and Discussion

The "forming process" is required to activate all of the Sn:SiO$_x$ RRAM devices, using dc voltage sweeping with a compliance current of 2 mA. The forming current of the Sn:SiO$_x$ RRAM devices after SCCO$_2$ treatment was lower than that of pretreatment devices [see Fig. 1(a)]. After the forming process, the electrical current–voltage properties of the Sn:SiO$_x$ devices were compared before and after SCCO$_2$ treatment [Fig. 1(b)]. The current of Sn:SiO$_x$ devices is reduced at 0.1-V reading voltage after SCCO$_2$ treatment.

To investigate the interesting phenomena, we analyzed the current conduction mechanism of the Sn:SiO$_x$ thin film with and without SCCO$_2$ treatment, as shown in Fig. 2. The current conduction in the high resistance state of the Sn:SiO$_x$ device was transferred to the Schottky emission from the Poole–Frenkel conduction after SCCO$_2$ treatment. These phenomena were attributed to the improvement of dielectric properties using SCCO$_2$ treatment, which have been reported in our previous study [9]. On the other hand, the carrier transport in the low-resistance state (LRS) of the Sn:SiO$_x$ device was dominated by ohmic conduction in the Sn:SiO$_x$ layer. According to the relationship of hopping conduction, $J = qNav_0 e^{-q\phi_T/kT} e^{qaV/2dkT}$, where N, a, ϕ_T, υ_0, and d are the density of space charge, the mean of hopping distance, the intrinsic vibration frequency, the barrier height of hopping, and the film thickness, respectively; the current conduction mechanism will transfer to hopping conduction because of the change of material properties after SCCO$_2$ treatment. Therefore, we utilized the material spectra analyses to find out the reason of the electrical transfer mechanism from ohmic conduction to hopping conduction.

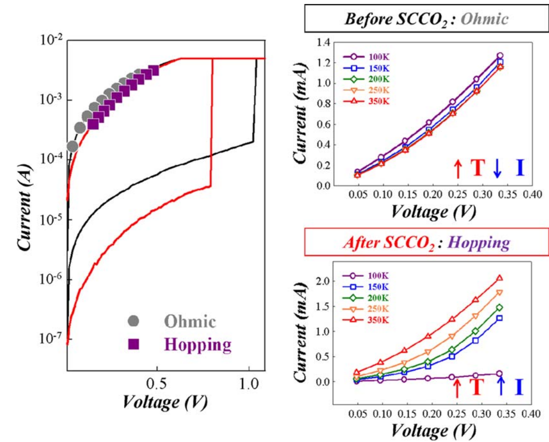

Fig. 2. Current conduction curves in the Sn:SiO$_x$ film before and after SCCO$_2$ treatment. The fitting of current curves for the Sn:SiO$_x$ film with and without SCCO$_2$ treatment was dominated by hopping conduction and Ohmic conduction mechanisms, respectively.

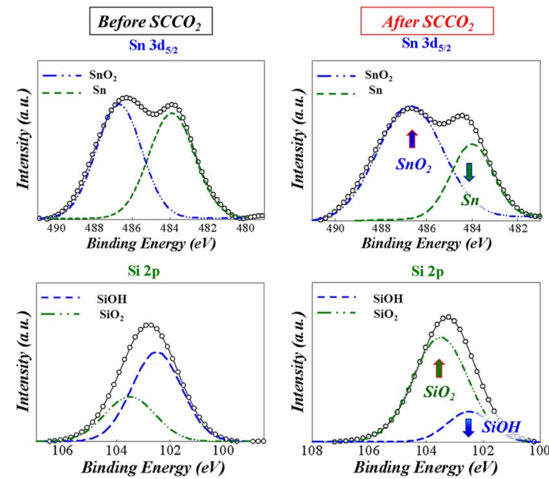

Fig. 3. XPS spectra of Sn 3d$_{5/2}$ and Si 2p core levels in the Sn:SiO$_x$ film before and after SCCO$_2$ treatment. The mole fraction of metallic tin and Si–OH bonds in the Sn:SiO$_x$ film are reduced obviously, but that of tin oxide and silicon oxide bonds are increased after SCCO$_2$ treatment.

Compared with the peak area of Sn, Si, and O XPS spectra, the mole fraction of Sn:Si:O in the cosputtered Sn:SiO$_x$ film was 0.3%:29.5%:70.2%. According to the XPS spectra analyses for the Sn 3d$_{5/2}$ core level (see Fig. 3), the mole fraction of Sn–O bond was greatly raised, but that of the Sn element was decreased in the Sn:SiO$_x$ thin film after SCCO$_2$ treatment. In addition, the mole fraction of the Si–O bond was substantially increased in contrast with that of the Si–OH bond after SCCO$_2$ treatment in terms of the XPS spectra analyses of the Si 2p core level. Therefore, the degree of oxidation would be increased, which is accompanied with dehydration in the SCCO$_2$-posttreated Sn:SiO$_x$ thin film.

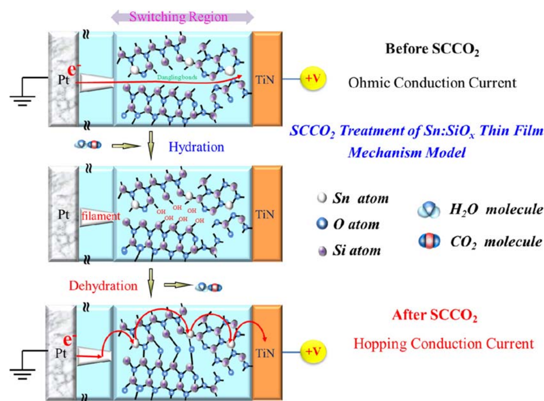

Fig. 4. Schematic of the carrier hopping effect in Sn:SiO$_x$ RRAM due to hydration–dehydration reaction mechanism through $SCCO_2$ treatment.

Based on the electrical and material analyses, we proposed a reaction model to explain the transfer of carrier conduction mechanism of the Sn:SiO$_x$ film with $SCCO_2$ treatment, as shown in Fig. 4. The conductive filament will be formed in the pretreatment Sn:SiO$_x$ film after the forming process. The conductive filament will be connected with a 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$_x$ film was put into the $SCCO_2$ fluid environment, the H_2O 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. The H_2O molecule was approached to grain boundary leading to the hydration reaction in the Sn:SiO$_x$ film. Then, monomolecular CO_2 in supercritical fluids induces the dehydration of neighbor hydroxyl groups to form Si–O–Si and Sn–O–Si cross-linking bonding in the film. Hence, the tin metal in the Sn:SiO$_x$ thin film will be isolated by $SCCO_2$ treatment. Only if the conductive filament formed in the Sn:SiO$_x$ film, the carrier will hop through the isolated tin metal in the switching region of the posttreated film. This phenomena will make the electrical current conduction in the LRS of the Sn:SiO$_x$ film to transfer from Ohmic conduction to hopping conduction.

IV. Conclusion

In conclusion, the current conduction mechanism of the LRS in the Sn-doped silicon oxide RRAM device is transferred to hopping conduction by supercritical fluid treatment. The water molecule can be brought into the film to crossly link the dangling bond of the grain boundary in the resistive switching layer by supercritical CO_2 fluid. In virtue of the phenomena, the tin metal of Sn:SiO$_x$ will be isolated by hydration–dehydration reaction of $SCCO_2$ fluids. Only if the conductive filament formed in the Sn:SiO$_x$ film, the electrical carriers of the RRAM devices with $SCCO_2$ fluid treatment will be transported through the isolated tin metal by hopping effect.

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