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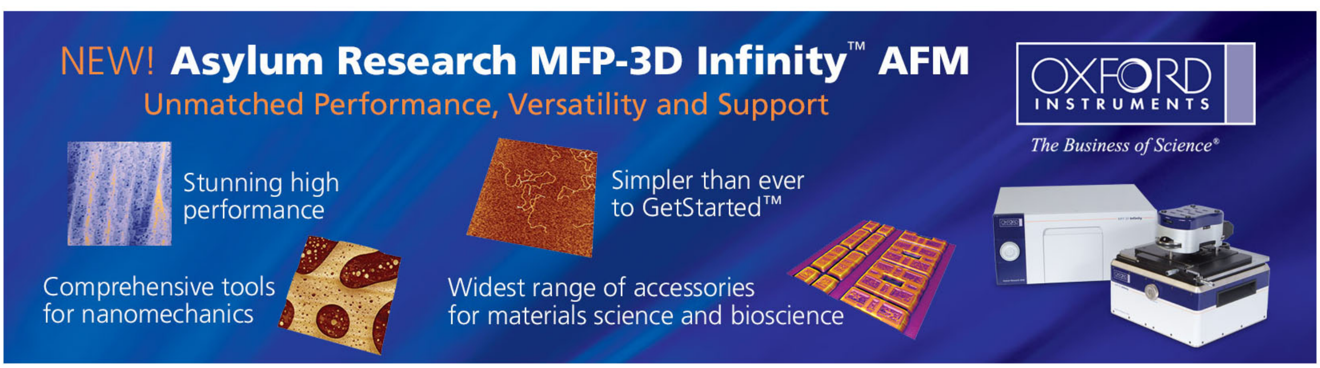

Dehydroxyl effect of Sn-doped silicon oxide resistance random access memory with supercritical CO_2 fluid treatment

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The tin-doped can supply conduction path to induce resistance switching behavior. However, the defect of tin-doped silicon oxide ($Sn:SiO_x$) increased the extra leakage path lead to power consumption and joule heating degradation. In the study, supercritical CO_2 fluids treatment was used to improve resistive switching property. The current conduction of high resistant state in post-treated $Sn:SiO_x$ film was transferred to Schottky emission from Frenkel-Poole due to the passivation effect. The molecular reaction model is proposed that the defect was passivated through dehydroxyl effect of supercritical fluid technology, verified by material analyses of x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4750235]

To overcome the technical and physical limitation issues of conventional charge storage-based memories,[1–4] the resistance random access memory (RRAM) composed of an insulating layer sandwiched by two electrodes is a great potential candidate for next-generation nonvolatile memory due to their superior properties such as low cost, simple structure, fast operation speed, and nondestructive readout.[5,6]

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), such as hydrogenated amorphous-silicon TFTs and ZnO TFTs.[7–13] The liquid-like and gas-like double properties of $SCCO_2$ fluids can be used to dissolve and transport H_2O molecules into the thin film and assist in oxidizing thin film at a low temperature. In addition, CO_2 is a nontoxic, nonflammable, and chemical-stable material. Although most RRAM devices have many superior properties of nonvolatile memory, the high operation current of RRAM during steady state is a major issue to nonvolatile memory for the application of portable electronic products. Therefore, the supercritical CO_2 is worthy to develop for improving the electrical properties of RRAM switching layer.

The tin-doped can supply conduction path to induce resistance switching behavior.[14] However, the defect of tin-doped silicon oxide ($Sn:SiO_x$) would increase the extra leakage path lead to power consumption and joule heating degradation. In this work, the resistive switching layer of Sn-doped silicon oxide ($Sn:SiO_x$) was treated by $SCCO_2$ fluids to enhance its electrical properties. The Pt/$Sn:SiO_x$/TiN sandwiched devices were fabricated to investigate resistive switching properties of $Sn:SiO_x$ after $SCCO_2$ treatment. In addition, the influence of $SCCO_2$ treatment on resistive switching behaviors of $Sn:SiO_x$ was evaluated by material and conduction mechanism analyses. Because the supercritical fluid has gaslike and high pressure properties to efficiently diffuse into nanoscale without damage,[15] the current of post-treated $Sn:SiO_x$ was reduced obviously due to the trap passivated by H_2O molecule of the $SCCO_2$ fluids.

The experimental samples were prepared as follows: the $Sn:SiO_x$ thin film (about 30 nm) was deposited on the TiN/Ti/SiO_2/Si substrate by co-sputtering with the pure SiO_2 and Sn targets. The sputtering power was fixed at RF power 200 W and 3 W for SiO_2 and Sn targets, respectively. The co-sputtering was carried out in argon ambient (Ar = 30 sccm) with a working pressure of 6 mTorr at room temperature. In contrast, the $Sn:SiO_x$ films were put into the reactive chamber of supercritical fluid system and then the $SCCO_2$ fluid mixed with 0.5 ml water were syringed into the reactive chamber to treat the sample. During the treatment, the water-mixed supercritical CO_2 fluids were heated and pressured to 120 °C and 3000 psi in the stainless steel chamber of supercritical fluid system for 1 h. Finally, the Pt top electrode of 200 nm thickness was deposited on $Sn:SiO_2$ film to form electrical devices with 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, 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.

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 $Sn:SiO_x$ RRAM devices after $SCCO_2$ treatment was lower than that of pre-treatment devices (Figure 1(a)). This phenomenon is attributed to the improvement on dielectric properties

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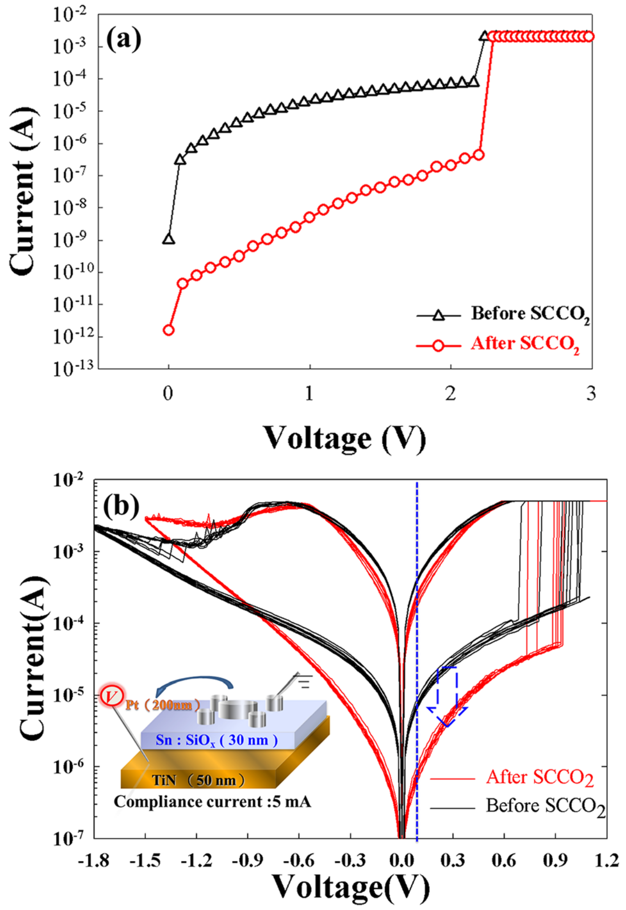

FIG. 1. (a) The forming current curves of the Sn:SiO_x RRAM devices before and after $SCCO_2$ treatment. (b) The black and red curves are the resistive switching characteristics of Sn:SiO_x film before and after $SCCO_2$ treatment, respectively. The current in high resistance state of post-treated Sn:SiO_x film is reduced about 15 times from 9 μA to 0.6 μA.

through $SCCO_2$ treatment, which has been reported by our previous study.[8] After the forming process, the electrical current-voltage properties of the Sn:SiO_x devices were compared before and after $SCCO_2$ treatment (Figure 1(b)). The current of Sn:SiO_x devices is reduced at 0.1 V reading voltage after $SCCO_2$ treatment. Figure 1(b) shows the electrical current-voltage (I-V) properties of the Sn:SiO_x RRAM devices before and after $SCCO_2$ treatment. We can find that the current of Sn:SiO_x in high resistive state (HRS) is reduced from 9 μA to 0.6 μA at 0.1 V reading voltage after $SCCO_2$ treatment. The interesting phenomenon indicates that the increment of operation resistance for readout is about 15 times after $SCCO_2$ treatment. To investigate the current reduction mechanism, we analyzed the current conduction mechanism in HRS of Sn:SiO_x with and without $SCCO_2$ treatment as shown in Figure 2. The relationship in the curve of ln(I/V) versus the square root of the applied voltage ($V^{1/2}$) is linear. According to the relationship of Frenkel Poole conduction, $I = \frac{qN_c\mu}{d}V\exp[\frac{q}{kT}(2\sqrt{\frac{qV}{4\pi\varepsilon_i d}} - \phi_{Bt})]$, where d, N_c, μ, ε_i, and ϕ_{Bt} are the insulator thickness, density of ionized traps, carrier mobility, dielectric permittivity, and trap barrier height, respectively. 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

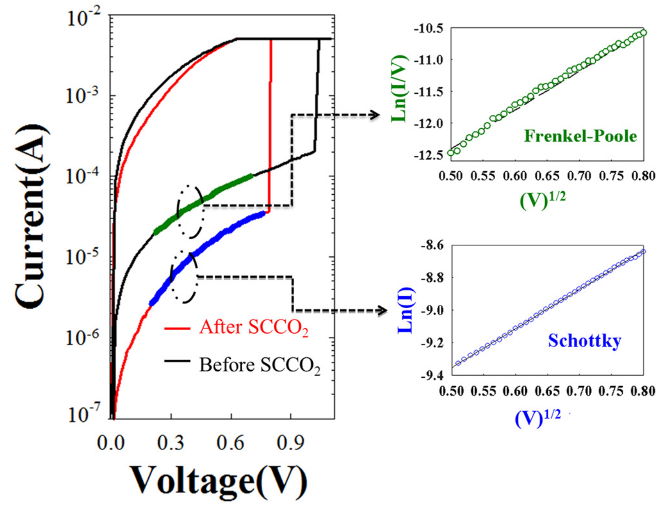

FIG. 2. The current conduction curves in the Sn:SiO_x film before and after $SCCO_2$ treatment.

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, $I = AA^*T^2\exp[\frac{q}{kT}(\sqrt{\frac{qV}{4\pi\varepsilon_i d}} - \phi_B)]$, where ϕ_B, d, A, and A* are the Schottky barrier height, film thickness, electrode area, and Richardson's constant for thermionic emission, respectively.[16] The results revealed that the carrier transport of Sn:SiO_x 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 electrical transfer mechanism from Frenkel Poole conduction to Schottky emission. Compared the FTIR spectra of Sn:SiO_x film with and without $SCCO_2$ treatment (Figure 3), 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_x 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

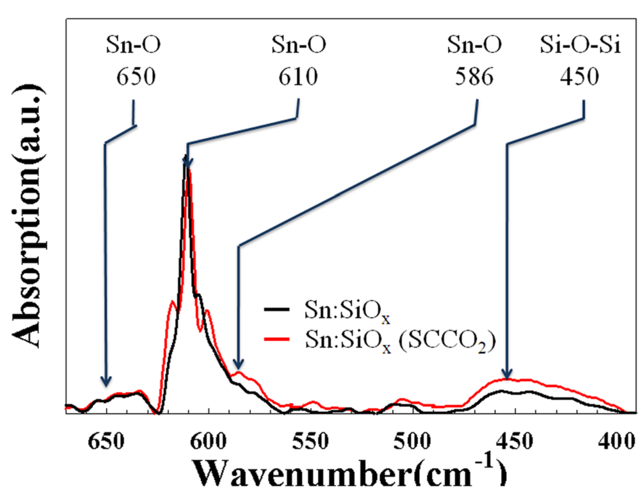

FIG. 3. The comparison of FTIR spectra of Sn:SiO_x film before and after $SCCO_2$ treatment. Both intensity of Sn-O and Si-O-Si bonds are increased in Sn:SiO_x film after $SCCO_2$ treatment.

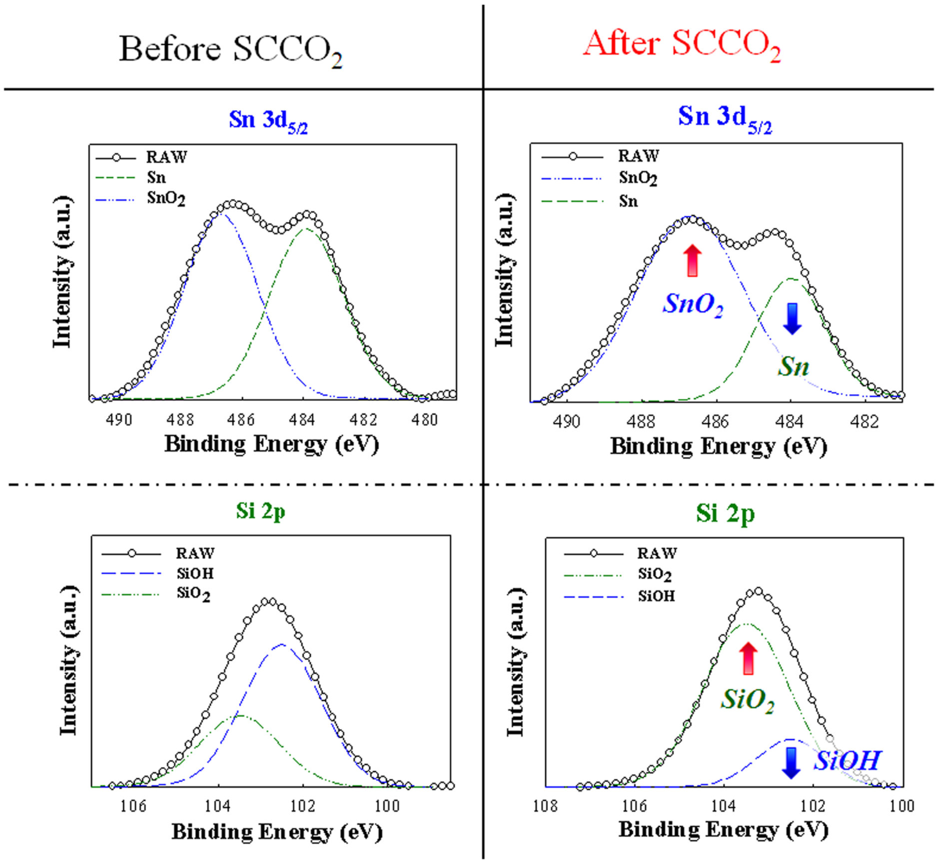

FIG. 4. XPS spectra of Sn $3d_{5/2}$ and Si 2p core levels in Sn:SiO_x film before and after $SCCO_2$ treatment. The mole fraction of metallic tin and Si-OH bonds in Sn:SiO_x film is reduced obviously but that of tin oxide and silicon oxide bonds is increased after $SCCO_2$ treatment.

content of silicon oxide bonding in the film also increased.[17] According to XPS spectra analyses for Sn $3d_{5/2}$ core level (Figure 4), the mole fraction of Sn-O bond was obviously risen but that of Sn element was decreased in Sn:SiO_x 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 Figure 4. Therefore, we infer that the level of oxidation would increase and accompany with dehydration in the post $SCCO_2$-treated film. These results were consistent with the above-mentioned FTIR analyses.

Based on the material analyses results, we proposed a reaction model to explain the current reduction mechanism of Sn:SiO_x film with $SCCO_2$ treatment as shown in Figure 5. As the sample was put into the water-mixed $SCCO_2$ fluid environment, the H_2O molecule was carried into the dangling bonds of amorphous Sn:SiO_x film by $SCCO_2$ fluid, which is attributed to the high penetration ability of $SCCO_2$ fluid. The H_2O molecule was approached to dangling bonds 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 so as to form Si-O-Si and Sn-O-Si cross-linking bonding in the film. Hence, the trap of Sn:SiO_x film can be passivated by $SCCO_2$ treatment, which can cause the electrical current conduction in HRS of Sn:SiO_x film transferred from Frenkel Poole conduction to Schottky emission. The phenomena will cause the improvement of dielectric

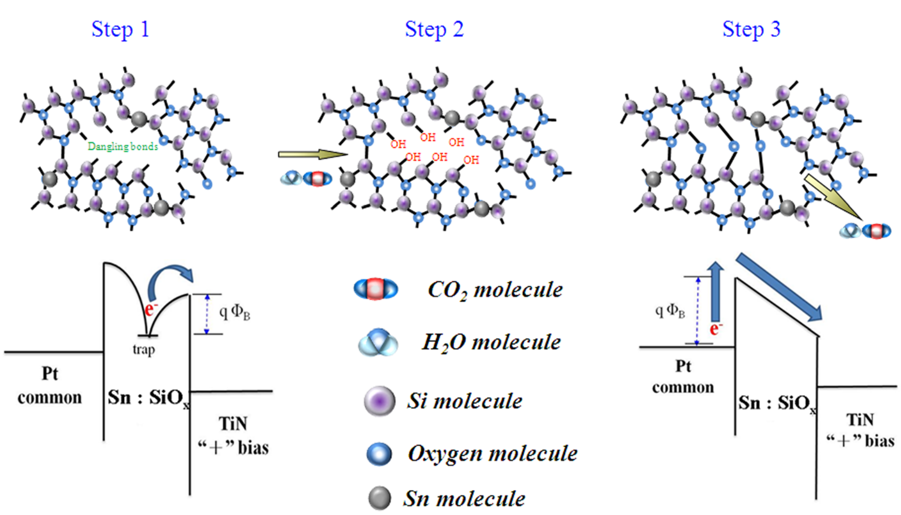

FIG. 5. The schematic diagram of passivation mechanism of $SCCO_2$ treatment on Sn:SiO_x film. The schematic structure for each step represents the situation of chemical bonding in the amorphous Sn:SiO_x film before and after $SCCO_2$ treatment.

properties of thin film, which is demonstrated by our previous study.[8]

In summary, the operation current of Sn-doped silicon oxide RRAM device was decreased by supercritical fluid treatment in this study. The water molecular can be brought into the film by supercritical CO_2 fluid, which induce dehydroxyl effect to passivate the dangling bond in the amorphous resistive switching layer. The operation resistance of RRAM can be increased due to the decrease of defect in the layer, which results in low power consumption. Therefore, supercritical fluid treatment can improve the properties of resistive switching layer of RRAM device.

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