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Electrical conduction mechanism of $Zn:SiO_x$ resistance random access memory with supercritical CO_2 fluid process

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In this study, the electrical conduction mechanism of $Zn:SiO_x$ resistance random access memory (RRAM) treated with supercritical CO_2 fluid ($SCCO_2$) process was investigated by low temperature measurement. The current of low resistance state for current-voltage curves in $SCCO_2$-treated and untreated $Zn:SiO_x$ RRAM were measured and compared under a low temperature range from 100 K to 298 K. The electrical conduction mechanisms of hopping conduction and metal-like behaviors in $SCCO_2$-treated and untreated $Zn:SiO_x$ RRAM were discussed, respectively. Finally, the electrical conduction mechanism was analyzed and verified by the chemical composition and bonding intensity of XPS analyses. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819162]

In recent years, portable consumer electronic products thrive, possessing greater need of nonvolatile memory, display, and integrated circuits (ICs).[1] Among different next-generation nonvolatile memories,[2–5] the resistance random access memory (RRAM) device is the most promising candidate because of its non-destructive readout,[6] low operation voltage,[7] high operation speed,[8] long retention time,[9] and simple structure.[10] Various materials were widely reported to reveal resistive switching behaviors for applications in RRAM devices, and silicon oxide is a promising material for RRAM applications because of its maturity and compatibility in IC processes.[11,12] Therefore, it is worthy of investigation for silicon-based oxide RRAM for the future mass production in memory industry.

Lately, the electrical and physical properties of various dielectric layer improved by the low temperature supercritical CO_2 ($SCCO_2$) fluid process have been investigated and demonstrated.[13] Material defects of dielectric can be passivized by $SCCO_2$ process because of its efficient penetration and damage-free diffusion ability in the microstructures of dielectric layer.[14]

In this work, zinc doped SiO_2 ($Zn:SiO_x$) by co-sputtering at room temperature was taken as the resistance switching layer of RRAM device. To discuss and explain the resistive switching mechanism of zinc-doped SiO_2 layer, the Pt/$Zn:SiO_x$/TiN device was fabricated with inert Pt as the top electrode. In addition, the temperature dependent current-voltage (I-V) curves and the voltage dependent activation energy for electrical conduction mechanism were discussed to explain the influence of the $SCCO_2$ process on $Zn:SiO_x$ resistive switching behaviors.

Metal-insulator-metal (MIM) RRAM devices, schematically shown in the inset of Fig. 1, was fabricated to investigate the electrical conduction mechanism of $SCCO_2$-treated $Zn:SiO_x$ RRAM. For MIM capacitor structure, the $Zn:SiO_x$ thin film (about 35 nm) was deposited on the patterned TiN/Ti/SiO_2/Si substrate by co-sputtering with the pure SiO_2 and Zn targets. After that, the $Zn:SiO_x$ thin film RRAM devices were placed in a supercritical fluid system at 150 °C for 2 h, and the process chamber was injected with 3000 psi $SCCO_2$ mixing with 0.3 volume percent pure H_2O. Finally, the Pt top electrode with a thickness of 200 nm was deposited on $Zn:SiO_x$ film to form Pt/$Zn:SiO_x$/TiN sandwich structure by DC magnetron sputtering. The I-V characteristics of the RRAM devices were measured by Agilent B1500 semiconductor parameter analyzer and Cascade M150 microprobe station.

Figure 1 shows the I-V curves of the $Zn:SiO_x$ RRAM device treated by low temperature $SCCO_2$ treatment method, and shown in the inset is the bipolar switching behavior by applying DC sweep bias on bottom TiN electrode. From the experimental result, we can observe that on state current of the $SCCO_2$-treated devices is lower than that of untreated devices. This phenomenon is attributed to the improvement on dielectric properties through $SCCO_2$ treatment, which has been reported in our previous study.[14]

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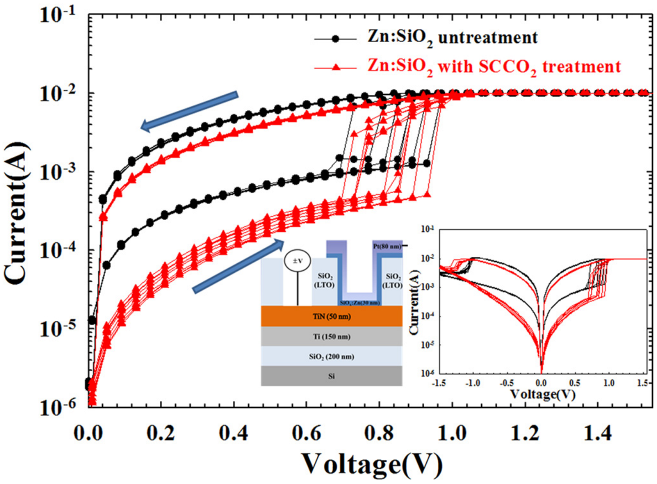

FIG. 1. The current-voltage (I-V) curves are the resistive switching characteristics of $Zn:SiO_x$ device with and without $SCCO_2$ treatment. The inset is a schematic diagram of $Zn:SiO_x$ device for electrical measurement and full sweep cycle.

To discuss and investigate the electrical conduction mechanism of on state current for $SCCO_2$-treated and untreated $Zn:SiO_x$ devices, the I-V curves of low resistance state (LRS) are measured and compared at vary temperature condition. Figure 2 shows the on state current of LRS of the $Zn:SiO_x$ RRAM device measured within a low temperature range from 100 K to 298 K. The on state current of the $Zn:SiO_x$ device measured at a temperature of 100 K is 0.52×10^{-2} A/cm^2 when the applied voltage is 0.3 V. However, we find that the on state current of $Zn:SiO_x$ device decreases to 0.44×10^{-2} A/cm^2 as the temperature rise to 298 K. As shown in the bottom right inset of Fig. 2, the linear relationship in the curve of ln(I) versus the reciprocal temperature (1/T) is found for the current of LRS state in untreated $Zn:SiO_x$ device. In addition, the current of LRS state decreases with the increase of temperature. This indicates that current conduction represents Ohmic conduction with metal-like behavior due to phonon scattering of the electrons transportation in the filament.[15] The Ohmic conduction with metal-like behavior in untreated $Zn:SiO_x$ thin film can be explained by accumulation of excessive metal phase zinc, which may lead to the formation of metallic filament. Ohmic conduction is further testified by current fitting, which was shown as the bottom left inset of Fig. 2.

Furthermore, we find that the on state current of $SCCO_2$-treated $Zn:SiO_x$ thin film RRAM device increases from 0.128×10^{-2} A/cm^2 to 0.142×10^{-2} A/cm^2 with an applied voltage of 0.3 V as the temperature increases from 100 K to 298 K (shown in Fig. 3). In addition, the current of LRS state in the $SCCO_2$-treated $Zn:SiO_x$ devices exhibits the hopping conduction behavior, which is shown in bottom left inset of Fig. 3. The hopping conduction of leakage current is due to the thermally excited electrons surpassing the energy barrier height (E_a) built by hetero-traps in dielectric,[16] which can be demonstrated by the linear relationship in the curve of ln(I) versus the reciprocal temperature (1/T) for the current of LRS. The relationship between ln(I) and 1/T is shown in the bottom right inset of Fig. 3.

To investigate the E_a for $SCCO_2$-treated $Zn:SiO_x$ devices, the Arrhenius plot of LRS is shown in Fig. 4. 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 E_a extracted from the Arrhenius plot is 0.058 eV. To the hopping conduction, the conduction current increases with temperature, and this is resulted from thermally excited electrons hopping from one trap state to another trap state in discontinuous metallic filament. In addition, the smaller E_a is due to the energy barrier lowering caused by trapped electrons jumping between the continuous potential well, which is formed by hetero-traps in $SCCO_2$-treated $Zn:SiO_x$ device.[16]

To verify the LRS of $SCCO_2$-treated $Zn:SiO_x$ device, whose conduction mechanism exhibits hopping behavior, the chemical composition and bonding are analyzed by X-ray photoelectron spectroscopy (XPS), and the result is shown in the inset of Fig. 4. The Zn-O binding energy intensity of

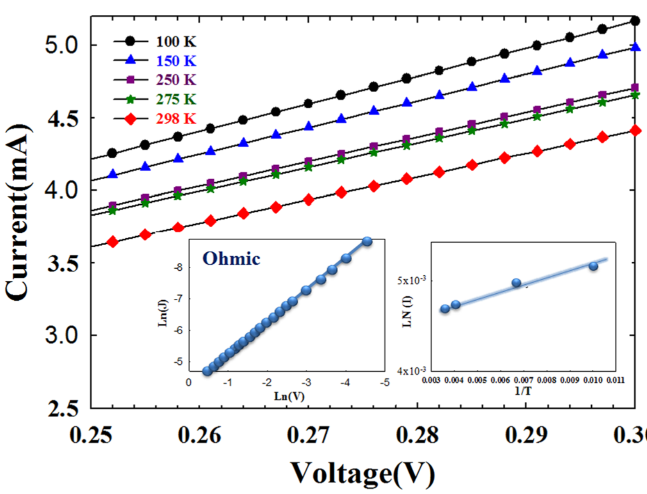

FIG. 2. The I-V curves of $Zn:SiO_x$ device measured at a low temperature range of 100 K to 298 K. The bottom right and left insets are the plot of ln(I) vs (1/T) in LRS of $Zn:SiO_x$ device and Ohmic conduction current fitting, respectively.

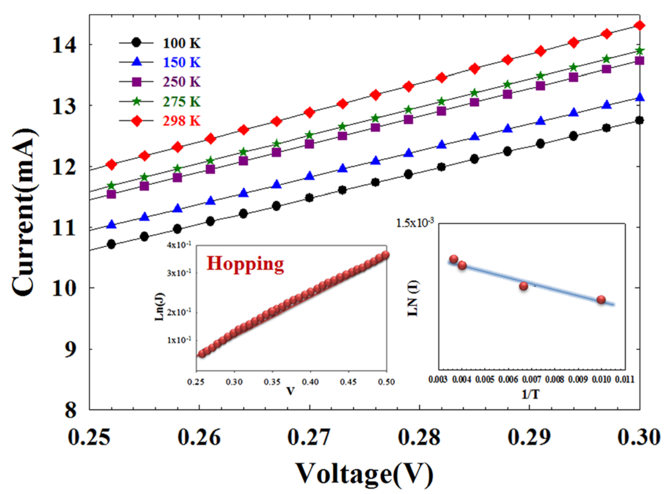

FIG. 3. The I-V curves of $SCCO_2$-treated $Zn:SiO_x$ device measured at a low temperature range of 100 K–298 K. The bottom right and left insets are the plot of ln(I) vs (1/T) in LRS of $SCCO_2$-treated $Zn:SiO_x$ device and Hopping conduction current fitting, respectively.

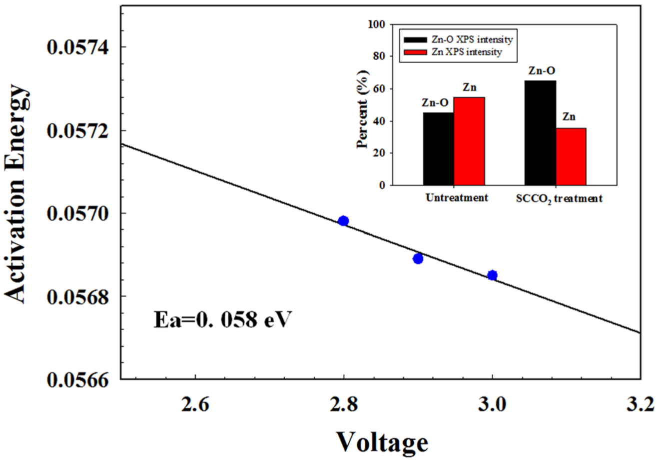

FIG. 4. The Arrhenius plot of the LRS in $SCCO_2$-treated $Zn:SiO_x$ device. The inset is the intensity comparison of Zn-O and Zn XPS spectra for $SCCO_2$-treated and untreated $Zn:SiO_x$ devices.

$SCCO_2$-treated $Zn:SiO_x$ device increases from 45.13% to 64.7%. In addition, the zinc binding energy intensity decreases from 54% to 35%. These results implicate that content of metal phase zinc in $SCCO_2$-treated $Zn:SiO_x$ device decreases, leading to the formation of discontinuous metallic filament in RRAM device. Therefore, the electrical conduction mechanism of $SCCO_2$-treated device is dominated by hopping conduction current, owing to the oxidation ability and passivation effect of $SCCO_2$.

In conclusion, the electrical conduction mechanisms of $SCCO_2$-treated and untreated $Zn:SiO_x$ RRAM device were investigated by low temperature measurement. According to the analyses of LRS state at vary temperature condition, the electrical conduction mechanism of $SCCO_2$-treated and untreated $Zn:SiO_x$ devices obeyed the hopping conduction and Ohmic conduction, respectively. The Ohmic conduction with metal-like behavior was caused by metallic filament, which was formed by excessive metal phase zinc in $Zn:SiO_x$ film. The hopping conduction resulted from the discontinuous metallic filament influenced by $SCCO_2$ treatment as $SCCO_2$ exhibited strong oxidation ability and passivation effect.

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