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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). Among different next-generation nonvolatile memories, the resistance random access memory (RRAM) device is the most promising candidate because of its non-destructive readout, low operation voltage, high operation speed, long retention time, and simple structure. 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. 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. Material defects of dielectric can be passivated by SCCO$_2$ process because of its efficient penetration and damage-free diffusion ability in the microstructures of dielectric layer.

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 Ti/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$_2$O. 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.
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 various temperature conditions. 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 $0.52 \times 10^{-2}$ 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 $0.44 \times 10^{-2}$ A/cm$^2$ as the temperature rises 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 $0.128 \times 10^{-2}$ A/cm$^2$ to $0.142 \times 10^{-2}$ 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, 

$$J = \frac{qN_a\tau_0 e^{-qE_a/KT}}{kT d} = \frac{qN_a\tau_0 e^{-qE_a/2 kdT}}{2 kT d},$$

where $N$, $a$, $\tau_0$, $E_a$, 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...
SCCO2-treated Zn:SiOx 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 SCCO2-treated Zn:SiOx device decreases, leading to the formation of discontinuous metallic filament in RRAM device. Therefore, the electrical conduction mechanism of SCCO2-treated device is dominated by hopping conduction current, owing to the oxidation ability and passivation effect of SCCO2.

In conclusion, the electrical conduction mechanisms of SCCO2-treated and untreated Zn:SiOx RRAM device were investigated by low temperature measurement. According to the analyses of LRS state at vary temperature condition, the electrical conduction mechanism of SCCO2-treated and untreated Zn:SiOx 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:SiOx film. The hopping conduction resulted from the discontinuous metallic filament influenced by SCCO2 treatment as SCCO2 exhibited strong oxidation ability and passivation effect.

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