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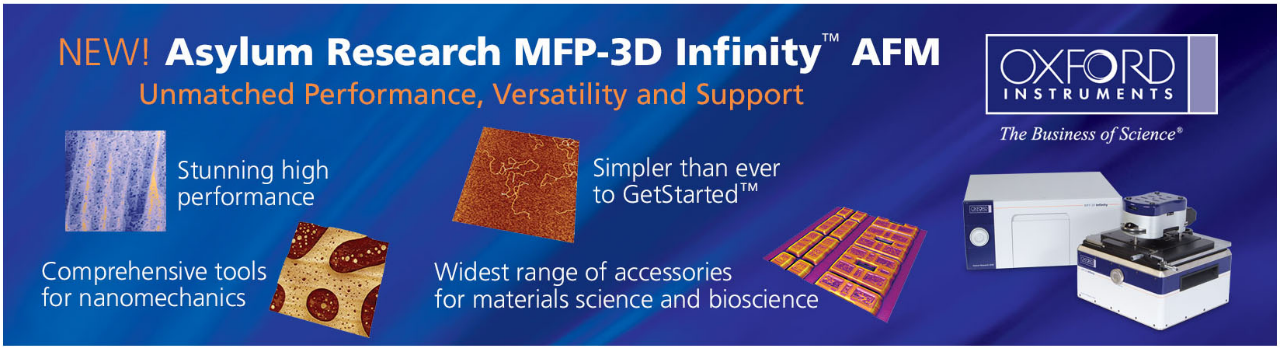

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Low temperature improvement on silicon oxide grown by electron-gun evaporation for resistance memory applications

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In this work, the supercritical CO_2 fluid mixed with cosolvents is introduced to terminate the traps in electron-gun (e-gun) evaporation deposited silicon oxide (SiO_x) film at 150 °C. After the proposed treatment, the SiO_x film exhibits a lower leakage current and a resistive switching behavior that is controllable by applying proper voltage bias. The change in resistance is over 10^2 times and the retention time attains to 2×10^3 s. It is also discovered that the resistive switching behavior seemingly relates to the amount of traps. © *2008 American Institute of Physics*.
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Since the first observation of bistable resistance states in the 1960s, reversible and reproducible resistive switching phenomena caused by applied electric field have been investigated widely to be used as resistive random access memories (RRAMs). In recent years, many metal oxides and perovskite oxides, such as Nb_2O_5, TiO_2, and Nb-doped $SrTiO_3$, had been reported for RRAM applications.[1–3] Nevertheless, there are only a few studies mentioning the process of producing RRAM at low temperature. In this study, the supercritical fluid (SCF) technology is introduced to fabricate resistive switching memory at 150 °C. The SCF is usually utilized to extract impurity, dehydrate, and dry materials with no damage.[4–6] It also has been applied to deliver oxidant into a metal oxide film to terminate electrical traps.[7,8] Due to the origin of bistable resistance states possibly caused by some kind of charge traps,[9,10] we would employ SCF technology to make the e-gun deposited oxide own bistable resistance states by varying the amount of traps.

The SiO_x films with an average thickness of 5–7 nm were directly deposited on *p*-type silicon wafers by e-gun evaporation system using a pure SiO_2 target. The chamber pressure and the substrate temperature were maintained at 2×10^{-6} torr and 25 °C, respectively. These SiO_x films were split into three groups and treated with different post-treatments. The first group was placed in a SCF system at 150 °C for 2 h, where it was full of 3000 psi supercritical CO_2 ($SCCO_2$) fluid. The second group was immersed into a pure H_2O vapor ambience at 150 °C for 2 h, in a pressure-proof stainless steel chamber. The third group was treated with cosolvent added 3000 psi $SCCO_2$ fluid (8 vol % ethyl alcohol and 2 vol % H_2O). The H_2O was taken as an oxidant to passivate electrical traps in SiO_x film. The ethyl alcohol played a role of surfactant between nonpolar $SCCO_2$ fluid and polar H_2O molecule for increasing the solubility of H_2O molecules in $SCCO_2$ fluid. After different treatments, the Al top electrode was thermally evaporated onto the surface of SiO_x through a circle-shaped shadow mask from the metal insulator semiconductor (MIS) structure. Finally, the Al bottom electrode was deposited onto the backside of *p*-type silicon wafers for the enhancement of voltage coupling. The electrical characteristics of MIS structure were measured by a HP 4156-A semiconductor analyzer.

Figure 1 shows the current density (J) of SiO_x film that was treated with pure 3000 psi $SCCO_2$ fluid; the bias voltage (V_G) was applied on top the electrode with a grounded bottom electrode. The plot of $\ln(J/E^2)$ versus the reciprocal of electric field $(1/E)$ for the current density in negative bias condition is displayed in the top right inset of Fig. 1. A linear dependence indicates that the trap-assisted tunneling (as the schematic band diagram in the bottom left inset of Fig. 1) dominated conduction mechanism while the negative bias was larger than –0.8 V.[11] The high leakage current reaching about 10^{-1} A/cm^2 implies that numerous traps are present in the e-gun deposited SiO_x film. In positive bias condition, the

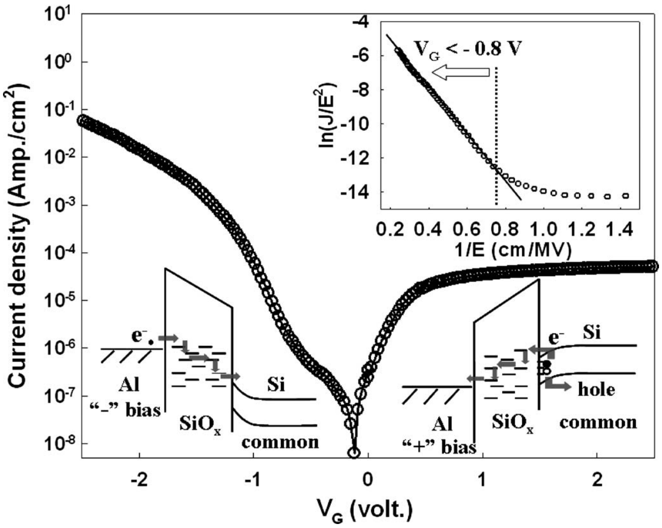

FIG. 1. Plot of current density (J) vs bias voltage for the SiO_x film that was treated with 3000 psi $SCCO_2$ fluid. Insets: (top right) the curve of $\ln(J/E^2)$ vs $(1/E)$ for the current density in negative bias condition, and (bottom left) the schematic band diagram of trap-assisted tunneling in negative bias condition, (bottom right) the schematic band diagram accounting for leakage current generated from interface states in positive bias condition.

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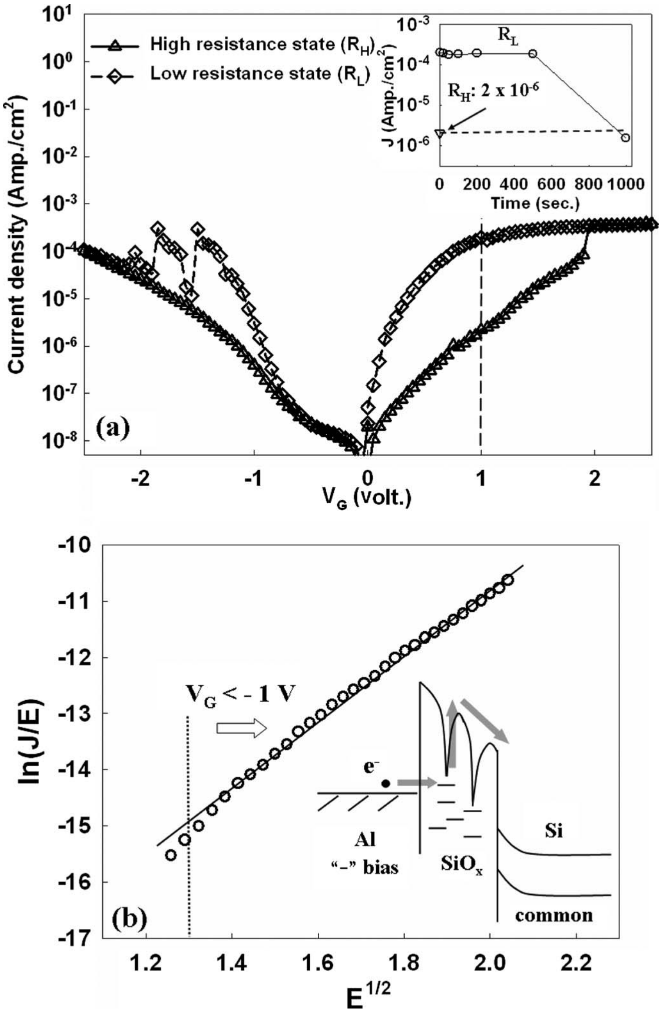

FIG. 2. (a) Current curves vs bias voltage for the SiO_x film that was treated with H_2O vapor. The inset shows the stability of the R_H state at reading voltage of 1 V. (b) Plot of $\ln(J/E)$ vs $(E^{1/2})$ for the current density of the high resistance state in negative bias condition. The inset shows the schematic band diagram describing the PF emission.

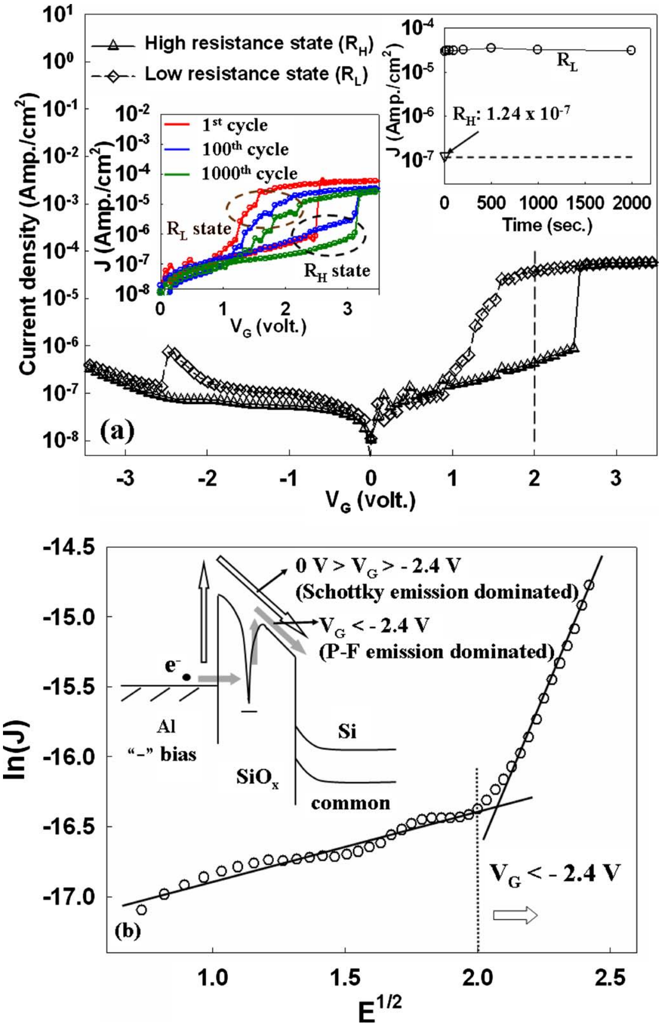

FIG. 3. (Color online) (a) Current curves vs bias voltage for the SiO_x film that was treated with cosolvent added 3000 psi $SCCO_2$ fluid. The insets show the stability of the R_H state at reading voltage of 2 V and the switching operations for 1, 100, and 1000 cycles. (b) Plot of $\ln(J)$ vs $(E^{1/2})$ for the current density of the high resistance state in negative bias condition. The inset shows the schematic band diagram including the SR emission (at low electric field) and PF emission (at high electric field).

electrons originate commonly from (1) the interface states, (2) traps in depletion region, and (3) bottom electrode of substrate.[12] In this work, the generation of electrons from the bottom electrode of substrate or the traps in the depletion region is negligible because the substrate is *p*-type single-crystal Si. Therefore, the saturatelike leakage current was generated mainly from the interface states (as illustrated in the bottom right inset of Fig. 1), and it was limited by the density of interface states and the carrier generation rate. This limitation caused a lower leakage current in positive bias condition. From these results, we revealed that the pure CO_2 molecule is ineffective to passivate traps.

The current curves of the H_2O vapor treated SiO_x film are shown in Fig. 2(a), and it expressed the high resistance state initially. Interestingly, this SiO_x film was detected to exhibit a resistive switching behavior between high resistance state (R_H) and low resistance state (R_L), and the resistance state is variable by applied bias voltage. The voltages of switching resistance state are about 1.9 (from R_H to R_L) and −1.8 V (from R_L to R_H). The maximum ratio of the two resistance states (R_H/R_L) is over 10^2 times, and the retention property of the R_H state at room temperature is displayed in the inset of Fig. 2(a). This phenomenon was never observed for the pure $SCCO_2$ fluid treated SiO_x film. Additionally, the leakage current was reduced obviously after H_2O vapor treatment. For realizing the reduction of leakage current, the current density of the high resistance state in negative bias condition was analyzed according to Poole–Frenkel (PF) emission, shown in Fig. 2(b). The linear trend indicates that the PF emission dominated conduction mechanism. The PF emission is owing to field enhanced thermal excitation of trapped electrons in insulator onto the conduction band.[13] The conversion of conduction mechanism from trap-assisted tunneling to PF emission demonstrates the reduction of traps, and it is attributed to the parts of traps in the SiO_x film that had been passivated by H_2O molecule during the H_2O vapor process.[14]

Figure 3(a) shows the current curves of the SiO_x film that was treated with cosolvent added 3000 psi $SCCO_2$ fluid. After this treatment, the SiO_x film also performed a resistive switching behavior with higher voltages of switching resistance state and longer retention time. Figure 3(b) shows the plot of $\ln(J/E)$ versus square root of applied electric field $(E^{1/2})$ for the current density of the high resistance state in

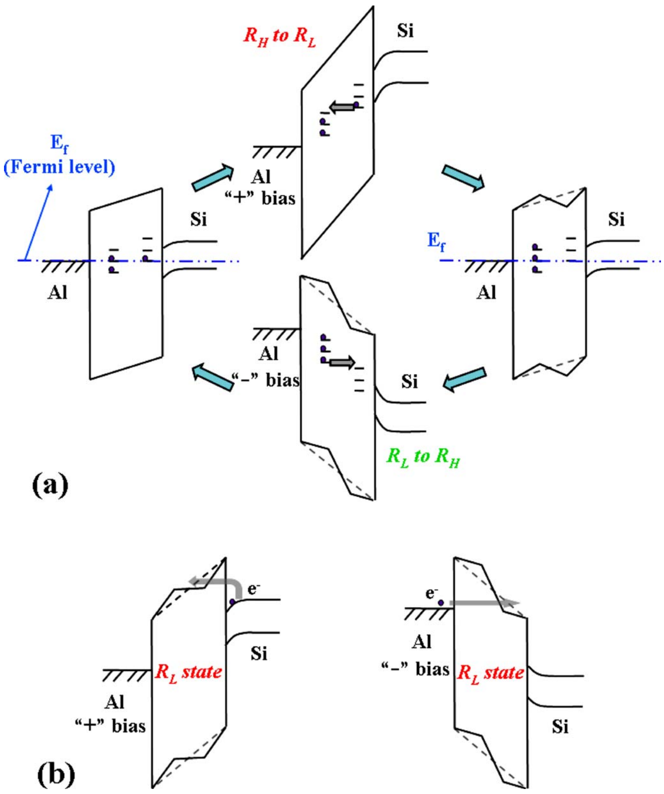

FIG. 4. (Color online) (a) A possible mechanism interpreting the resistive switching behavior. (b) The conduction mechanism in positive/negative bias condition with twisted band diagram (R_L state), where the dash line is the original band diagram (R_H state).

negative bias condition. The two-slope linear dependence indicates that the conduction mechanism was dominated by Schottky–Richardson (SR) emission at low electric field and then dominated by PF emission while the negative bias was larger than −2.4 V. The SR emission is independent of traps and caused by electron exciting thermally across the potential energy barrier via field assisted lowering at a metal–insulator interface.[15] The low leakage current of 10^7 A/cm^2 expresses that the traps were further terminated, i.e., the SCCO$_2$ fluid owns superior capability of delivering H_2O molecule into SiO$_x$ layer than H_2O vapor. Although the PF emission occurred at high electric field, a few traps remained, but the proposed SCCO$_2$ treatment is still sufficient to improve the quality of the SiO$_x$ film.

From the above results, the resistive switching behavior is apparently associated with the amount of traps. The authors infer that the resistance variation perhaps resulted from the movement of carrier in the SiO$_x$ gap,[9] and the possible diagram mechanisms are shown in Figs. 4(a) and 4(b). Applying a positive bias enough to cause the tunneling of electrons in the SiO$_x$ gap, the energy band diagram would twist and lead to the change of resistance state from R_H to R_L. Applying a negative bias enough to make these electrons tunnel back, the resistance state would return from R_L to R_H. If there are numerous traps present in the SiO$_x$ gap, such as a pure SCCO$_2$ fluid treated sample, these electrons might tunnel back without external bias, and thereby no change in resistance is observed. On the other hand, if there are only a few traps present in the SiO$_x$ gap, it is required to apply a higher bias to shift the electrons, and a superior retention is expected. Thus, in comparison with H_2O vapor treated sample, the SiO$_x$ film treated with cosolvent added SCCO$_2$ fluid performs higher bias voltages of switching resistance state and longer retention time.

In summary, the preliminary improvement on the e-gun deposited SiO$_x$ film was obtained after H_2O vapor treatment as a result of passivating traps by H_2O molecules. A further study also demonstrated that the trap passivation efficiency is optimized by the treatment of the SCCO$_2$ fluid mixed with ethyl alcohol and H_2O, because SCCO$_2$ fluid could more effectively carry H_2O molecule into the SiO$_x$ layer. Besides, the reduction of traps would induce a reversible resistive switching behavior. This phenomenon possibly resulted from the movement of carrier in the SiO$_x$ gap, so the amount of traps would influence the bias voltages of switching resistance state and the retention time. By the proposed SCCO$_2$ technology, it is promising for e-gun deposited SiO$_x$ to achieve a full low temperature fabrication of resistive memory.

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