

Research Article

Resistive Switching Characteristics of a SiO_x Layer with CF_4 Plasma Treatment

Chih-Yi Liu,¹ Yueh-Ying Tsai,¹ Wen-Tsung Fang,² and Hung-Yu Wang¹

¹ Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 807, Taiwan

² Department of Physics, National Kaohsiung Normal University, Kaohsiung 824, Taiwan

Correspondence should be addressed to Chih-Yi Liu; cyliau@cc.kuas.edu.tw

Received 9 December 2013; Revised 8 February 2014; Accepted 8 February 2014; Published 11 March 2014

Academic Editor: Sheng-Po Chang

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A 20 nm SiO_x layer is deposited using radio-frequency sputtering to form the resistive switching layer of a $\text{Cu}/\text{SiO}_x/\text{Pt}$ memory device. The SiO_x -based device demonstrates the resistive switching characteristics with an electrochemical reaction. CF_4 plasma treatment was used to modify the SiO_x layer and incorporate fluorine atoms into the SiO_x layer. The bombardment damage and fluorine incorporation caused the SiO_x film to form a stack-like structure. This reduced the operating voltage and improved switching dispersion. The fluorine repaired the Cu/SiO_x interface, thus increasing the barrier height of the Cu/SiO_x interface and the resistance of the high resistance state. A statistical analysis of the conducting filament formation was performed in order to evaluate the number of formation/rupture sites. The resistive switching of the CF_4 -treated sample had higher possibility to use the same filament sites; thus, the CF_4 -treated sample had stable resistive switching behavior.

1. Introduction

Recently, nonvolatile memory (NVM) has become an important device for portable products. Several novel technologies have been proposed to develop an advanced device as the next generation of NVM. Resistive random access memory (RRAM) has attracted significant interest due to its simple structure, high switching speed, and low operating voltage [1]. RRAM devices can be reversibly switched between a high resistance state (HRS) and a low resistance state (LRS) by DC voltages or voltage pulses. The resistance change can be used to store information for NVM applications. The resistive switching behavior is primarily influenced by the material groups [2, 3], electrodes [4], and interface status [5, 6]. In general, the switching mechanisms of these resistive switching behaviors can be divided into three groups: thermochemical reactions [7], electrochemical reactions [8–10], and the valence change effect [11]. However, a detailed switching mechanism is still lacking. Several studies [12–14] proposed the surface effect on the resistive switching behaviors, which indicated that oxygen or humidity may influence the redox reaction in the interface or resistive layer. Although a RRAM

device has many promising advantages, the resistive switching behavior is unstable and may cause operation failure. Therefore, several methods such as nanoparticle [15], stacked layers [16], and process optimization [17] have been proposed to improve the switching dispersion. Plasma treatments have also been proposed to improve switching dispersion [18, 19]. Wang et al. proposed the CF_4 plasma treatment to improve the resistive switching properties with the valence change effect [19]. The CF_4 plasma treatment changed the Schottky barrier height to reduce the operating voltages. However, the effect of plasma treatment on an electrochemical-based RRAM has not been studied.

This study adopted Cu and SiO_x materials to fabricate a RRAM device in order to integrate them with the complementary metal-oxide-semiconductor (CMOS) process. In this study, a $\text{Cu}/\text{SiO}_x/\text{Pt}$ structure was fabricated to investigate the resistive switching behavior of an electrochemical RRAM device. CF_4 is a common molecule used in the CMOS etching process. CF_4 plasma treatment has been used previously to improve the Si/SiO_2 interface of a MOS structure [20]. In this study we adopted the CF_4 plasma treatment to modify the SiO_x layer and investigated its effect

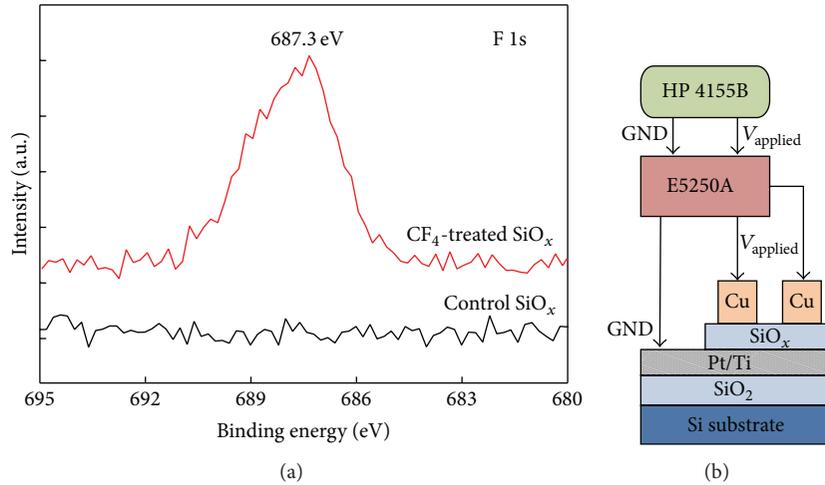


FIGURE 1: (a) The XPS results of the control and CF_4 -treated films and (b) the measurement configuration of the conducting filament formation.

on the resistive switching behavior of a $\text{Cu}/\text{SiO}_x/\text{Pt}$ device. The CF_4 plasma treatment reduces the operating voltage and improves the switching dispersion. The bombardment damage and fluorine incorporation should be responsible for the switching dispersion improvement.

2. Experimental Procedure

A 20 nm SiO_x film was deposited on a Pt-coated substrate (Pt/Ti/ SiO_2 /Si) in a pure Ar ambient using a radio-frequency sputter at room temperature. The related information of the SiO_x film can be found in our previous study [21]. A 200 nm Cu top electrode was deposited using a thermal evaporation technique to form a $\text{Cu}/\text{SiO}_x/\text{Pt}$ structure (control sample). The top electrode area, as defined by the metal mask, was $5 \times 10^{-5} \text{ cm}^2$. A 30 nm SiO_x film was also deposited on a Pt-coated substrate. CF_4 plasma treatment of 25 W was used to etch the SiO_x film back to a 20 nm SiO_x film and incorporate fluorine atoms into the SiO_x film. Next, a 200 nm Cu film was deposited to form the Cu/CF_4 -treated SiO_x/Pt structure (CF_4 -treated sample). As shown in Figure 1(a), the result of X-ray photoelectron spectroscopy (XPS, JAMP-9500F, JEOL) spectra of the CF_4 -treated SiO_x film indicates that fluorine atoms were incorporated into the SiO_x layer. The electrical measurements were performed using an HP 4155B semiconductor parameter analyzer and an Agilent E5250A low-leakage switch mainframe at room temperature. The bias voltage was applied on the Cu top electrode of a single device and the bottom electrode was grounded in order to measure the current-voltage characteristics. To prevent the influence of surface effect, all electrical measurements were performed in the air ambient with 60% relative humidity. In Figure 1(b) the measurement configuration of the conducting filament formation is shown. Two devices were connected in parallel forming a single pair and were stimulated by the same electrical signal at the same time. A small read voltage (0.05 V) was used to measure each device's resistance. The formation statistics and reuse probability were calculated

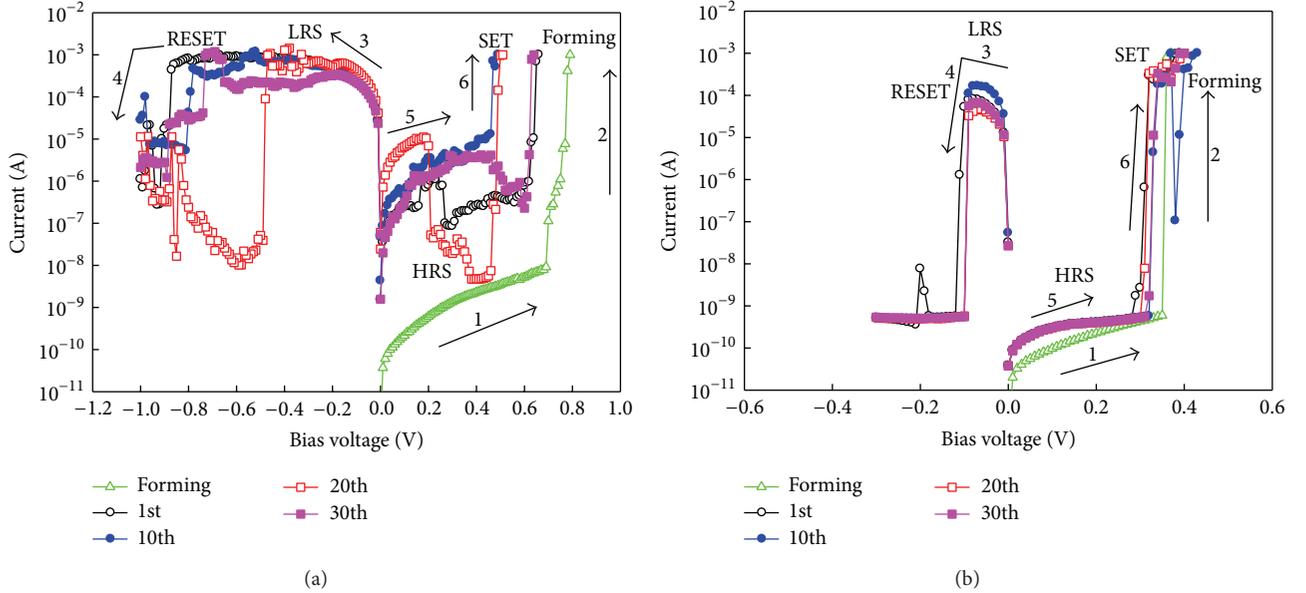
with 10 pairs, with each pair having 100 successive switching cycles.

3. Results and Discussion

In Figure 2(a) 30 successive resistive switching cycles of the control sample are shown. The device current abruptly increases by a forming process in the positive polarity stage. The device current is abruptly decreased by a RESET voltage when the polarity is negative and increases again by a SET voltage in the positive polarity. The device current can reversibly switch between a HRS and a LRS by DC voltages in various polarities. A compliance current of 1 mA was used to prevent permanent damage during the forming and SET processes. The current-voltage characteristics were unstable during the voltage sweeping. The resistance states and the operating voltages showed a large dispersion. Figure 2(b) shows 30 successive resistive switching cycles of the CF_4 -treated sample. Its resistive switching was more stable than that of the control sample. Compared with the control sample, the SET and RESET voltages of the CF_4 -treated sample were almost identical. According to the switching mechanism of the conducting filament model with the electrochemical reaction, a positive voltage is applied to the Cu electrode during the SET process. The Cu metal is dissolved into Cu ions, and then Cu ions drift across the SiO_x film to the Pt electrode. Then, the Cu ions reduce and electrodeposit on the Pt electrode. Next, a Cu conducting filament grows to connect the Cu and Pt electrodes, and thus the resistive state is switched to the LRS. A negative voltage is applied to the Cu electrode during the RESET process, and the part of the conducting filament near the Cu/SiO_x interface is dissolved to rupture the conducting filament and thus the resistive state is switched to the HRS. Fitting curves of ohmic conduction for the LRS current-voltage characteristics of the control sample and the CF_4 -treated sample indicate that the LRS exhibited linearly ohmic behaviors with slopes of 0.982 and 0.981, respectively [22]. The LRS conduction mechanisms of

TABLE 1: The statistical results of the conducting filament formation for the control and CF₄-treated samples.

| | After forming process | | Multiple filament | SET process | |
|---------------------------------|-----------------------|------------|-------------------|------------------|-----------|
| | Type | Percentage | | Reuse difference | Reuse sum |
| Control sample | Single | 50% | 1.5% | 94.8% | 97.7% |
| | Multiple | 50% | 7.9% | 49.3% | 88.9% |
| | Total | 100% | 4.7% | 72.0% | 93.3% |
| CF ₄ -treated sample | Single | 100% | 0.4% | 95.4% | 96.8% |

FIGURE 2: (a) Resistive switching behaviors of the control sample and (b) resistive switching behavior of the CF₄-treated sample. Numbers and arrows denote the sequence.

the two samples were consistent with the conducting filament model.

In Figure 3(a), the statistical analysis of the operating voltages of the two samples is shown. The magnitudes of the operating voltages of the CF₄-treated sample were smaller than those of the control sample. In addition, the CF₄-treated sample had smaller voltage dispersion than the control sample. This improvement in voltage dispersion can simplify circuit design and prevent operation failure. Figure 3(b) shows the statistical results of the device resistance of the control and CF₄-treated samples. The LRS resistance of the two samples was almost identical due to the same compliance current [23]. The XPS result from Figure 1(a) indicates that fluorine atoms were incorporated into the SiO_x film. Fluorine can repair the dangling bonds within the SiO_x film; thus, the Cu/SiO_x interface status improves. To prevent the disturbance of Cu dissolution into the SiO_x layer, the current-voltage characteristics of the HRS were measured at negative polarity. The formula of the Schottky emission [21] can be expressed as

$$J = A^* * T^2 * \exp\left(\frac{q\sqrt{qE/4\pi\epsilon_i}}{kT} - \frac{q\Phi_B}{kT}\right), \quad (1)$$

where J is the current density, A^* is the effective Richardson constant, T is the temperature, q is the elementary charge, k

is the Boltzmann constant, E is the electric field, Φ_B is the barrier height, and ϵ_i is the insulator dynamic permittivity. According to the fitting results, the HRS conduction mechanism of the two samples was dominated by the Schottky emission. The Schottky barriers of the control and CF₄-treated samples were 0.77 eV and 0.81 eV, respectively. Hence, the HRS resistance of the CF₄-treated sample was larger than that of the control sample. In addition, the HRS of the CF₄-treated sample had smaller dispersion than that of the control sample. Therefore, the CF₄-treated sample had a much higher switching margin than the control sample. Figure 4 shows the endurance characteristics of the two samples. The control sample showed large switching dispersion. Many soft errors could be found during successive switching cycles. The endurance cycle of the control sample was less than 1000, while the CF₄-treated sample showed stable switching cycles and an endurance cycle of over 2500.

To further understand the formation of conducting filaments within the SiO_x film, two devices had the same sweep voltage applied at the same time (Figure 1(b)), while their resistance was recorded. Table 1 shows the statistical results of the conducting filament formation. In some situations, the conducting filament can be found in only one device, which is known as single-filament switching. In another case, the conducting filament can be found in

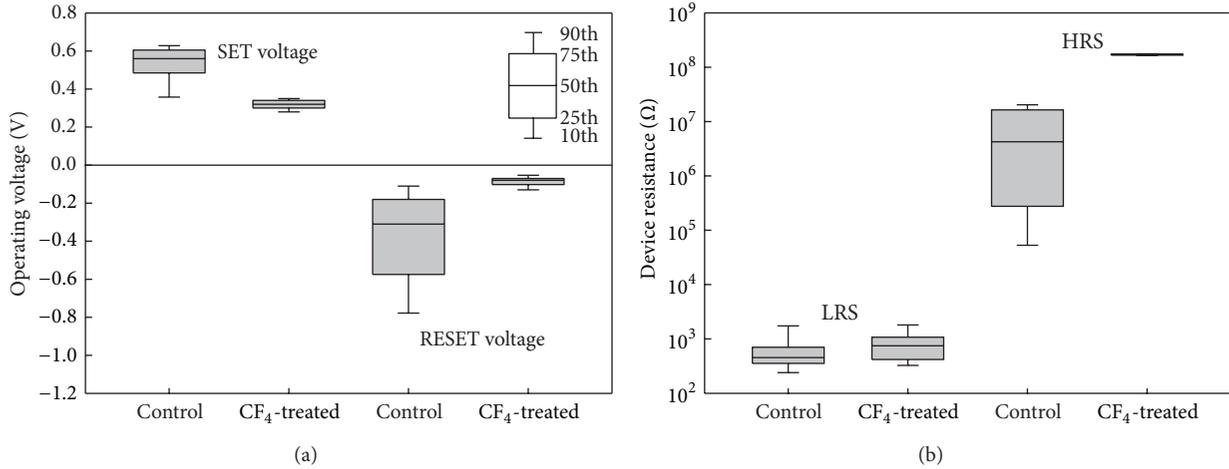


FIGURE 3: (a) The operating voltage of the control and CF₄-treated samples and (b) the device resistances of the control and CF₄-treated samples.

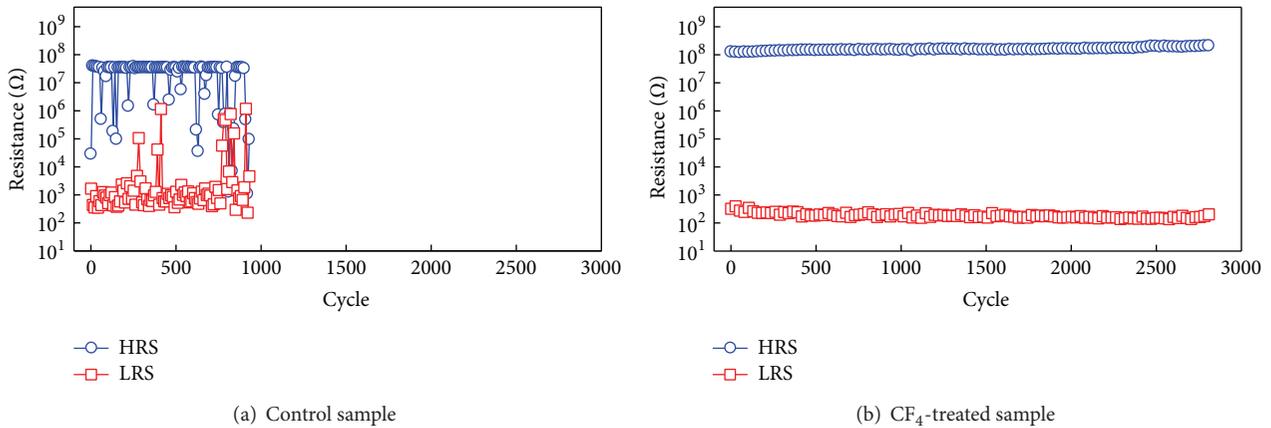


FIGURE 4: The endurance characteristics of the control and CF₄-treated samples.

both devices at the same time. Based on logical reasoning, there should be more than two conducting filaments in this pair, which was called multiple-filament switching. After the forming process, the control sample had 50% single-filament and 50% multiple-filament cases. In comparison, the CF₄-treated sample had 100% single-filament cases. Multiple-filament switching means that the device may switch via different conducting filaments. The control sample had 4.7% multiple-filament switching during the successive switching cycles, which indicated that multiple conducting filaments existed, which could cause complex formation/rupture of conducting filaments. In comparison, the CF₄-treated sample only had 0.4% multiple-filament switching, which showed a more stable switching behavior. The definition of reuse is the conducting filament formed in the same device as the previous cycle. The reuse difference is the difference of the reuse in the two devices. The reuse sum is the total reuse in the pair. The CF₄-treated sample had a larger reuse difference and reuse sum than the control sample, which indicated that the conducting filaments within the CF₄-treated sample had higher possibility to be formed at the same sites. Therefore,

the CF₄-treated sample displayed a more stable resistive switching behavior.

The CF₄-treated SiO_x film was bombarded with ions, which may cause more traps in the near-surface of the SiO_x film than in the lower region [24]. The traps within the SiO_x layer would increase the Cu diffusion coefficient. In Figure 1(a) it can be seen that the fluorine atoms were incorporated into the SiO_x film. Fluorine incorporation could decrease the dielectric constant of the SiO₂ layer [20]. Therefore, the dielectric constant of the near surface was smaller than that of the lower region. According to Gauss' law, the electrical field in the near surface was larger than that in the lower region. Therefore, the formation/rupture of the Cu filament would be confined within the near surface, which decreased the operating voltage and improved the switching dispersion. In addition, the HRS and LRS retention times of the CF₄-treated sample were more than 10⁴ s at room temperature. The CF₄-treated sample had a small operating voltage, stable resistive switching, high resistance ratio, high endurance, and long retention time. These factors mean that the device is an ideal candidate for the next-generation of NVM.

4. Conclusions

The influence of CF_4 plasma treatment on the resistive switching behavior of a $\text{Cu}/\text{SiO}_x/\text{Pt}$ structure was investigated. The ion bombardment and fluorine incorporation in the near-surface of the SiO_x film caused the SiO_x film to become a stack-like structure, which confines the formation/rupture in the near surface. Therefore, the CF_4 plasma treatment decreased the operating voltage and improved the switching dispersion. A statistical analysis of conducting filament formation was calculated to explain the resistive switching behavior using single-filament or multiple-filament switching. The CF_4 -treated sample had a larger probability of single-filament switching than the control sample. Therefore, resistive switching of the CF_4 -treated sample almost always occurred through the same filament, giving rise to the smaller switching dispersion.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors thank the National Science Council of R.O.C. for their financial supports under Project no. NSC 101-2221-E-151-044 and the facility support from National Nano Device Laboratories.

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