Effects of a Cu\textsubscript{x}O Buffer Layer on a SiO\textsubscript{x}-Based Memory Device in a Vaporless Environment

Chih-Yi Liu\textsuperscript{*} and Zheng-Yao Huang

Abstract

The resistive switching characteristics of the Cu/SiO\textsubscript{x}/Pt structure (control sample) exhibited a direct correlation to humidity. The H\textsubscript{2}O vapor formed the Cu oxide at the Cu/SiO\textsubscript{x} interface, and Cu ions were injected from the Cu oxide into the SiO\textsubscript{x} layer, thus improving the resistive switching. However, the control sample demonstrated substantial switching dispersion in a vaporless environment. The Cu\textsubscript{x}O layer in the Cu/Cu\textsubscript{x}O/SiO\textsubscript{x}/Pt structure (Cu\textsubscript{x}O sample) helped the dissolution of Cu ions from the Cu electrode into the SiO\textsubscript{x} layer, enabling effective electrochemical resistive switching in a vaporless environment. The Cu\textsubscript{x}O sample exhibited low switching dispersion and favorable endurance characteristics in a vaporless environment.

Keywords: Cu\textsubscript{x}O; Resistive switching; SiO\textsubscript{x}

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Background

Recently, resistive random access memory (RRAM) has attracted considerable interest because of its non-volatile resistance change in simple metal/insulator/metal structures [1, 2]. Depending on the material group [3], device structure [4, 5], and defect status [6, 7], various switching behaviors can be observed. The switching mechanisms are typically classified as either a valence change effect [8], a thermochemical effect [2, 9], or an electrochemical effect [10, 11], whereby distinct surface effects can be attributed to various mechanisms [12, 13]. Ke et al. proposed that the oxygen concentration influences the redox reaction in ZnO resistive switching [12], and Tsuruoka et al. suggested that H\textsubscript{2}O vapor plays an essential role in the redox reaction of an electrochemical Cu/SiO\textsubscript{2}/Pt device [13, 14]. The effects of moisture on Cu/SiO\textsubscript{2}/Pt and Cu/Ta\textsubscript{2}O\textsubscript{5}/Pt devices were different due to different adsorption coefficients of water. H\textsubscript{2}O vapor formed a Cu oxide interface between the Cu electrode and the oxide layer after the forming process and also enhanced Cu migration within the oxide layer. The H\textsubscript{2}O vapor facilitates in the dissolution of Cu ions into the SiO\textsubscript{2} layer, enabling effective resistive switching. The Cu/SiO\textsubscript{2}/Pt device does not perform the resistive switching without H\textsubscript{2}O vapor [13, 14]. However, there is no H\textsubscript{2}O vapor within a packaged chip, and this is a serious concern, because these devices are used in memory applications.

In this study, a Cu\textsubscript{x}O layer was inserted between the Cu and SiO\textsubscript{x} layer to improve the electrochemical resistive switching and minimize switching dispersion in a vaporless environment.

Methods

A 20-nm-thick SiO\textsubscript{x} layer was deposited on a Pt-coated substrate (Pt/Ti/SiO\textsubscript{2}/Si) using radio frequency sputtering at room temperature. Subsequently, a 200-nm-thick Cu electrode was deposited using a thermal evaporator at room temperature, to form the final Cu/SiO\textsubscript{x}/Pt structure (control sample). The device area was 5 \times 10^{-5} \text{ cm}^2. To create the Cu/Cu\textsubscript{x}O/SiO\textsubscript{x}/Pt structure (Cu\textsubscript{x}O sample), an additional 1-nm Cu\textsubscript{x}O layer was deposited on the SiO\textsubscript{x} layer by using a thermal evaporator at room temperature. The structures of the control sample and the Cu\textsubscript{x}O sample are illustrated in Fig. 1, respectively. X-ray photoelectron spectroscopy (XPS; PHI-5000, ULVAC-PHI) was used to analyze the composition of the Cu\textsubscript{x}O layer. The electrical measurements were performed using an HP 4155B semiconductor parameter analyzer, and the measurements were taken in both air (60 % relative humidity) and N\textsubscript{2} environments at room temperature. The bias
voltage was applied on the top electrode while the bottom electrode was grounded.

**Results and Discussion**

Figure 2 depicts the XPS Cu $2p_{3/2}$ spectra of the Cu$_x$O layer. The detailed chemical structure information was extracted through deconvolution of Cu $2p_{3/2}$ peaks, which showed a CuO peak locating at 934 eV and a Cu$_2$O peak locating at 932.6 eV. The Cu$_x$O layer is the mixture of CuO and Cu$_2$O. Figure 3 shows the resistive switching characteristics of the control and the Cu$_x$O samples in both air and N$_2$ environments. A positive-forming voltage was used to initialize the resistive switching; the resistance state was then switched from an initial resistance state (IRS) to a low resistance state (LRS). Following this transition, a negative Reset voltage was applied to switch from the LRS to a high resistance state (HRS). Subsequently, using a positive Set voltage, the HRS was switched back to a LRS. The device resistance can be reversibly switched between a LRS and a HRS by a Set voltage and a Reset voltage. Figure 3c, d illustrates the resistive switching characteristics of the Cu$_x$O sample in air and N$_2$ environments, and the behaviors were similar to those of the control sample in air. According to our previous study [15], device structure, and switching behavior, the resistive switchings of the control sample in air and the Cu$_x$O sample in both environments are dominated by the electrochemical model with a Cu conducting filament. However, as shown in Fig. 3b, the control sample in the N$_2$ environment required substantially higher operating voltages. The control sample in the N$_2$ environment also showed a reversible unipolar switching, and the temperature coefficient of LRS resistance was negative. Therefore, the switching mechanism should be the thermochemical effect with conducting filaments of oxygen-related defects.

Tsuruoka et al. proposed that a Cu/SiO$_2$/Pt structure exhibits no resistive switching in a vacuum or N$_2$ environment (no H$_2$O vapor) because of the desorption of residual water from the SiO$_2$ layer [13]. Because the composition of the SiO$_x$ film influences the switching mechanism [16], the result of this study in N$_2$ differed from the result of Tsuruoka et al., which may be due to the dissimilar composition between SiO$_x$ and SiO$_2$ layers. Although there was some difference between Tsuruoka’s study and our control sample in N$_2$, these two samples both performed unfavorably because of a lack of humidity and exhibited no electrochemical resistive switching. Because no copper oxide was formed at the Cu/SiO$_x$ (or SiO$_2$) interface of these two samples, no electrochemical resistive switching was observed. The Cu ion concentrations were calculated using the cyclic voltammetry (CV) method [17], and the results are presented in Fig. 4. The CV method is used to study the redox reaction of Cu within the device. The applied voltage swept to 0.15 V and then swept back until the current was zero. During this sweeping period, oxidized Cu ions were injected into the SiO$_x$ thin film. The amount of Cu ions ($Q$) can be calculated, and then, Cu ion concentration ($C_{ion}$) can be determined by the formula $C_{ion} = \frac{Q}{qN_AV}$, where $N_A$ is Avogadro’s number and $V$ is the device volume. The Cu$_x$O sample contained higher Cu ion concentrations than those in the control samples. In addition, the two samples contained larger Cu ion concentrations in air than in N$_2$. Tsuruoka
et al. proposed that H$_2$O molecules would form a hydrogen-bond network at grain boundaries in SiO$_2$ \[13\] and thus had larger Cu ion concentration. Therefore, the humidity and Cu$_x$O layer both help the dissolution of Cu ions into SiO$_2$ layer. The electrochemical resistive switching has three rate-limiting processes \[13\]: the Cu ionization at the Cu/SiO$_2$ interface, the migration of Cu ions in the SiO$_2$ film, and the nucleation of Cu at the Pt bottom electrode. In this study, the Cu nucleation at Pt electrode would not the rate-limiting process. The control sample in N$_2$ had the lowest Cu ion concentrations, and it cannot show an electrochemical resistive switching, which means that the Cu ionization at the Cu/SiO$_2$ interface is the rate-limiting process in N$_2$. Willis and Lang \[18\] proposed the three possible mechanisms for the Cu ionization at the Cu/SiO$_2$ interface under a positive applied voltage: the anodization-like process that Cu atoms are injected directly into the SiO$_2$ layer by the dissolution reaction \[Cu \rightarrow Cu^{2+} + 2e^-\], Cu ions injected into the SiO$_2$ from the Cu$_x$O formed at the Cu/SiO$_2$ interface due to reduction of the SiO$_2$, and the chemical oxidation of Cu atoms at the Cu/SiO$_2$ interface via H$_2$O, O$_2$, or out-gassing of the oxide \[13\]. In this study, the Cu/SiO$_2$/Pt cannot electrochemically switch in N$_2$. Therefore, the former two mechanisms should be excluded.

Figure 5a–c depicts the operating voltages of the two samples in both environments. The control sample in N$_2$ exhibited the highest operating voltages because of the lowest Cu ion concentration within the SiO$_2$ layer. Both samples exhibited lower operating voltages in air, as the H$_2$O vapor increased the Cu ion concentration in the SiO$_2$ layer. Tappertzhofen et al. proposed that there was no copper oxide at Cu/SiO$_2$ interface before the forming process, but the copper oxide was found after the forming process in air \[14\]. In addition, this electrochemical oxidation was not observed in anhydrous atmosphere. We also fabricated a Ni (200 nm)/Cu$_x$O...
(1 nm)/SiO$_x$ (20 nm)/Pt structure (not shown) which did not have an electrochemical resistive switching. This means that the 1-nm Cu$_x$O interlayer did not provide enough Cu ions to form Cu conducting filaments. Since the Cu electrode cannot be directly ionized to be Cu ions and a 1-nm Cu$_x$O interlayer does not provide enough Cu ions to form Cu conducting filaments, the possible explanation is that the Cu metal is transformed into immediate states of Cu oxide via the Cu$_x$O layer and then Cu ions can be injected from these immediate states by a positive electric field. Since the copper oxide cannot be electrochemically formed without a moisture environment, a Cu$_x$O layer in this study was deposited between the Cu and SiO$_x$ layers to solve this issue. The deposited Cu$_x$O layer also can help the dissolution of Cu ions from the Cu electrode into the SiO$_x$ layer, thus increasing the Cu ion concentration in the SiO$_x$ layer. This increase in the Cu ion concentration effectively reduced the forming and Set voltages. Figure 5d–f shows the device resistances in both air and N$_2$. The LRS conduction of the two samples in air and N$_2$ exhibited ohmic behavior. The LRS resistances were approximately determined according to the current compliance during the Set process. The two samples exhibited lower LRS resistances in air, which may be due to an increased Cu ion concentration in the SiO$_x$ layer during the Set process [8]. This increased concentration of Cu ions caused a formation of wider conduction filaments. The IRS and HRS conductions of the two samples were dominated by the Schottky emission (not shown). The two samples exhibited lower IRS resistances in air because of a lower Schottky barrier height. All switching parameters of the Cu$_x$O sample had larger variation in N$_2$ than in air. H$_2$O molecules would form a hydrogen-bond network at grain boundaries in SiO$_2$ [13] and thus enhanced Cu migration in the SiO$_x$ layer. Therefore, the Cu$_x$O sample had larger Cu ion concentration in air than in N$_2$. The supply of Cu ions influenced the operating voltages and

![Fig. 5](image) The parameters of resistive switching of the two samples. a The forming voltage. b The Set voltage. c The Reset voltage. d The IRS voltage. e The LRS resistance. f The HRS resistance.
the stability to grow Cu conducting filaments. Hence, the Cu$_x$O sample had a lower Cu ion concentration in N$_2$ and thus had larger variation in switching parameters.

Figure 6 shows the endurance characteristics of the two samples in both environments. The control sample in N$_2$ exhibited the least favorable endurance characteristics, because of its non-optimized thermochemical switching. Both of the samples exhibited a more favorable endurance in air than in N$_2$, which indicated that H$_2$O vapor increased the Cu ion concentration and thus improved the resistive switching. In a packaged chip, the RRAM device must switch in an environment without H$_2$O vapor. The Cu$_x$O sample demonstrated favorable endurance for more than 2000 cycles in the N$_2$ environment, demonstrating that it is suitable for RRAM applications.

Conclusions

This study investigated the addition of a Cu$_x$O layer to a Cu/SiO$_x$/Pt structure for maintaining the electrochemical resistive switching capabilities in a vaporless environment. The Cu ionization at the Cu/SiO$_x$ interface is the rate-limiting process for the electrochemical resistive switching in N$_2$. Therefore, Cu/SiO$_x$/Pt cannot have an electrochemical resistive switching in N$_2$. Therefore, in the Cu/Cu$_x$O/SiO$_x$/Pt structure, the Cu$_x$O layer helped the dissolution of Cu ions from the Cu electrode into the SiO$_x$ layer, effectively minimizing the switching dispersion. The Cu/Cu$_x$O/SiO$_x$/Pt also exhibited favorable endurance characteristics in a vaporless environment, demonstrating that it is suitable for practical applications.

Abbreviations

HRS: high resistance state; IRS: initial resistance state; LRS: low resistance state; RRAM: resistive random access memory; XPS: X-ray photoelectron spectroscopy.

Competing Interests

The authors declare that they have no competing interests.

Authors’ Contributions

CYL designed the experiment, participated in the result analysis, and wrote the paper. ZYH prepared the devices and carried out the material analysis and electrical measurements. Both authors read and approved the final manuscript.

Authors’ Information

CYL is an associate professor in the Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Taiwan. ZYH is a master student in the Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Taiwan.

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Fig. 6 Endurance characteristics in different measurement environments. a The control sample in air. b The control sample in N$_2$. c The Cu$_x$O sample in air. d The Cu$_x$O sample in N$_2$. 
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