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Resistive Switching Behavior of Partially Anodized Aluminum Thin Film at Elevated Temperatures

Wei Zhu, T. P. Chen, Ming Yang, Student Member, IEEE, Yang Liu, and S. Fung

Abstract—Resistive switching behavior of partially anodized aluminum thin film has been investigated at temperatures of 25 °C–250 °C. Both the reset and set voltages decrease with increasing temperature, showing Arrhenius-like dependence with small activation energies. The pulse voltage experiment also suggests that the conductive filament breaking/reconnection is easier to occur at a higher temperature. Some possible mechanisms for the phenomena are discussed. On the other hand, at elevated temperatures without continuous electric field applied, while the high-resistance state exhibits no significant change with time, the low-resistance state (LRS) shows a continuous degradation, and there is a sudden failure. The LRS failure time shows Arrhenius dependence with an activation energy of ~1.3 eV, suggesting that the LRS failure could be due to the migration of the excess Al atoms at high temperatures.

Index Terms—Aluminum oxide, resistive random access memory, resistive switching.

I. INTRODUCTION

RESISTIVE random access memory based on resistive switching in metal oxides is emerging as one of the most promising candidates for the next generation of non-volatile memory due to its superior performance such as fast switching speed, low operating voltage, simple structure, and great scalability potential. Resistive switching in various metal oxides such as NiO, TiO$_2$, Cu$_2$O, and ZnO has been frequently reported [1]–[4]. Resistive switching and conduction instability in aluminum oxide films, which can be easily fabricated with different techniques such as sputtering [5], atomic layer deposition [6], [7], O$_2$ plasma oxidation [8], and anodization [9]–[14], have also been observed. Most of the studies on resistive switching were carried out at room temperature, and there are relatively few studies at elevated temperatures [15]–[20]. In this paper, we have conducted a study of resistive switching behavior of a partially anodized aluminum thin film at elevated temperatures. Both the reset and set voltages decrease with increasing temperature, exhibiting Arrhenius dependence. The pulse voltage experiment also suggests that the conductive filament (CF) breaking/reconnection is easier to occur at a higher temperature. At elevated temperatures without the application of continuous electric fields, while the high-resistance state (HRS) exhibits no significant change with time, the low-resistance state (LRS) shows a sudden failure after certain time, and the failure time exhibits Arrhenius dependence.

II. EXPERIMENT

A 500-nm Al thin film was deposited on a supporting silicon substrate which was thermally oxidized to form a 10-nm silicon dioxide layer prior to the Al thin film deposition. The Al thin film deposition was carried out by dc sputtering of an Al target with purity of 99.99%. Anodization of the Al thin film was undertaken in a 0.15-M/L solution of oxalic acid at 25 °C, by applying a constant voltage of 40 V using a Keithley 2400 source meter with a 2 × 2 cm$^2$ platinum mesh as the cathode. The anodizing time was about 2 h. The thickness of the aluminum oxide layer formed by the anodization is about 30–50 nm. The X-ray photoelectron spectroscopy analysis indicates that the aluminum oxide layer is an Al-rich Al$_x$O$_y$ layer. This means that the oxide layer contains unreacted Al phase. After the anodization, another 300-nm Al thin film was deposited on the anodized aluminum film by electron beam evaporation to form the top electrode. Thus, a circular metal–insulator–metal (MIM) structure of Al layer/Al-rich Al oxide/unreacted Al layer was fabricated. The $I$–$V$ measurements on the fabricated structure were carried out with a Keithley 4200 semiconductor characterization system with a current compliance of 100 mA at different temperatures ranging from 25 °C to 250 °C.

III. RESULT AND DISCUSSION

Fig. 1(a) shows the repeated $I$–$V$ measurements at temperatures of 25 °C and 125 °C. The $I$–$V$ measurements were carried out by voltage sweeping starting from 0 V with a step of 1 mV. Both reset and set switchings can be observed during the voltage sweeping. When the voltage reaches the reset voltage ($V_{reset}$), the current drops from a large current (e.g., ~$10^{-2}$ A) to a much lower current (e.g., ~$10^{-7}$ A), i.e., the resistance of the MIM structure is switched from an LRS to an HRS. The HRS can be maintained until the voltage reaches the set voltage ($V_{set}$) at which the resistance is switched.

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Fig. 1. Resistive switching in $I-V$ measurements. (a) Repeated $I-V$ measurements. (b) $I-V$ measurements after $10^4$ set/reset cycles. (c) $I-V$ measurements for different device areas. (d) $I-V$ measurements with forward and backward voltage sweepings at 25 °C.

back to LRS. As can be observed in Fig. 1(a), the temperature has a significant effect on the reset and set voltages and the currents at the LRS and HRS as well. Both the $V_{\text{reset}}$ and $V_{\text{set}}$ at 125 °C are significantly lower than those at 25 °C. As the temperature increases, the currents at the LRS decrease, showing the metallic behavior, while the current at the HRS increases, showing the semiconductor behavior [17].

The aforementioned switching behavior and temperature dependence are also observed after $10^4$ set/reset cycles, as shown in Fig. 1(b). The $V_{\text{reset}}$ and $V_{\text{set}}$ measured from the voltage sweeping experiment as functions of the number of set/reset cycles that the device has experienced are shown in Fig. 2. It can be concluded from Fig. 2 that the set/reset cycling does not cause large device degradation. To examine the influence of the device area, three devices (circular shape) with diameters of 200 (small pad), 300 (medium pad), and 400 µm (large pad) were characterized. The $I-V$ characteristics of the set/reset switching of the three devices at low (25 °C)/high (125 °C) temperatures are shown in Fig. 1(c). The currents and set/reset voltages changed randomly in the repeated $I-V$ measurements for different pad areas, and no obvious area dependence was observed for the three devices. On the other hand, the $I-V$ measurement of forward voltage sweeping is also compared with that of backward voltage sweeping, as shown in Fig. 1(d). As can be observed in the figure, the switching from LRS to HRS occurred at 0.46 and 0.60 V for the forward and backward sweepings, respectively. However, the reset voltage for the forward sweeping could be randomly higher or lower than that for the backward sweeping, showing the fact that the resistance switching is a random event.

Temperature dependence of both $V_{\text{reset}}$ and $V_{\text{set}}$ has been measured on ten devices in the temperature range of 25 °C–200 °C, and the result is shown in Fig. 3. It can be observed in Fig. 3(a) that both $V_{\text{reset}}$ and $V_{\text{set}}$ significantly decrease with increasing temperature. Note that the change in the voltage drop in the contacts and metal connection at a current lower than 100 mA with temperature is insignificant because there is no large change in both the contact resistance and the Al film resistance. For example, the contact resistance values at 20 °C and 120 °C are estimated to be 3.45 and 3.35 Ω, respectively (the contact resistance is estimated with the following method: the resistance between two pads is measured as a function of the spacing between the two pads, and the contact resistance of the two pads can be obtained by extrapolating to zero pad spacing). The significant reductions in $V_{\text{reset}}$ and $V_{\text{set}}$ imply that the CF is easier to be formed and ruptured at a higher temperature. The phenomenon of decrease of set/reset voltage with temperature was also observed on HfO$_x$ thin film [20].
Fig. 3. (a) Temperature dependence of the reset and set voltages. (b) Arrhenius plots of the reset and set voltages measured before and after $10^4$ reset/set cycles.

The actual mechanism responsible for the resistive switching in the partially anodized aluminum thin film is not known yet. As such, an explanation to the switching behaviors at elevated temperatures is speculative in nature. Nevertheless, a plausible discussion on the temperature effect on the switching is given in the following. According to the joule heating reset model, the decrease of the $V_{\text{reset}}$ with temperature could be explained as follows: In the reset process, a higher ambient temperature makes more thermal energy produced by the joule heating to be dissipated in the CFs, and thus, the CFs are easier to break up [3], [18]. It was also suggested that, as temperature increases, both the probability to create oxygen vacancies and the oxygen ion mobility increase; therefore, a reduced electrical field (and, thus, a lower reset/set voltage) is required to break/reconnect the CFs in the reset/set process [20]. The situation could be explained as follows. In the set process, the electrical field can cause oxygen ions to be removed from their original lattice, leading to the oxygen-vacancy-related filament formation; in the reset process, oxygen ions can move to the oxygen vacancy sites, making the filament broken. Therefore, the creation of oxygen vacancies and the movement of the oxygen ions to the oxygen vacancy sites could play a dominant role in the set and reset processes, respectively. As both processes can be enhanced by temperature, a lower reset/set voltage is required at a higher temperature.

On the other hand, the electrochemical reactions, including oxidation and reduction, involved in the reset/set process could be also enhanced at a higher temperature, leading to a lower reset/set voltage. Therefore, multiple mechanisms could be responsible for the observed temperature dependence of the reset and set voltages shown in Fig. 3(a). If a thermally activated process such as solid-state diffusion/migration and electrochemical reactions is involved in the set/reset process, Arrhenius behavior could be observed. Fig. 3(b) shows the Arrhenius plots of the set and reset voltages measured on ten devices. As can be observed in Fig. 3(b), although there could be more than one mechanism involving in the set and reset processes, the average values of the set and reset voltages are approximately proportional to $\exp\left(E_s/kT\right)$, where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $E_s$ is an activation energy related to the set/reset process. The activation energies for both set and reset voltages are about the same ($\sim 50–60$ meV). In other words, both the set and reset switchings have similar small activation energies. The physics for the small activation energies is not clear yet. The temperature dependence of the average values of the set and reset voltages after $10^4$ reset/set cycles is also shown in Fig. 3(b). There are no large changes in both temperature dependence and values of the set and reset voltages after the $10^4$ reset/set cycles, indicating that the reset/set cycling does not have a large impact on the reset/set process.

Temperature-enhanced reset/set switching is also observed in the pulse voltage experiment. Fig. 4 shows the influence of temperature on the set/reset switching of one device under various pulse voltages/pulsewidths. As can be observed in the figure, stable switching (i.e., the device can switch to the opposite resistance state definitely), unstable switching (i.e., the device has a probability to stay in its current resistance state), and no switching (i.e., the device keeps in its current
retention behaviors of the LRS and HRS at 25 °C and 200 °C. resistance state without conduction transitions) can be observed, depending on the pulse voltage, pulselength, and temperature. Obviously, a higher pulse voltage facilitates the set/reset switching to occur in a shorter time. On the other hand, the pulse voltage/pulselength required for a stable switching is smaller at a higher temperature, showing that thermal energy can significantly enhance the set/reset switching triggered by a voltage pulse.

Fig. 5 shows the retention experiment of the LRS and HRS at 25 °C and 200 °C. At 25 °C, both the HRS and LRS exhibit no significant change within the time limit ($10^5$ s) of the experiment; however, at 200 °C, while the HRS also exhibits no significant change, the LRS shows a continuous degradation with time, and there is an abrupt increase (by approximately two orders) in its resistance after $\sim 2 \times 10^4$ s. Such situation is regarded as a retention failure as it is difficult to distinguish the LRS from the HRS now. It is worth to mention that the reading voltage (0.2 V) is small and is applied only during the reading operation. In addition, the duration of the reading operation is $\sim 1 \mu$s, which is too short to change the device state at a voltage of 0.2 V. Therefore, the effect of the reading voltage on the retention behaviors can be ignored.

Fig. 6 shows the Arrhenius plot of the LRS retention failure time ($t_{\text{LRS-failure}}$). The Arrhenius behavior can be expressed as

$$t_{\text{LRS-failure}} \propto \exp \left( \frac{E_a}{kT} \right)$$  \hspace{1cm} (1)

where $E_a$ is the activation energy for the LRS failure. The $E_a$ value yielded from the Arrhenius plot is $\sim 1.3$ eV, which is much larger than the activation energies of the set/reset process occurring during the voltage sweeping. The Arrhenius behavior of the LRS failure time with the large activation energy suggests that the LRS failure could be due to the dissolution of some CFs caused by the migration of the excess Al atoms at high temperatures without the application of continuous electric fields. It is worth to point out that the reset/set process in the voltage sweeping or pulse voltage experiments is caused by an applied electric field while there is no electric field involved during the retention periods. The mechanisms for the CF breaking/reconnection in the reset/set process should be different from that for the LRS failure in the retention experiment because the former are triggered by an electric field but the latter does not involve an electric field. This argument is supported by the fact that the activation energies for the former are much lower than that of the latter. On the other hand, as shown in Fig. 6, a retention time of 30 years can be achieved at 85 °C, which is long enough for a practical nonvolatile memory application. It is also worthy to mention that the LRS failure is permanent if there is no further set operation. However, the device with the LRS failure can be set and reset again, and the situation of the set/reset switching is similar to that before the LRS failure. Fig. 7 shows the set/reset switching at 25 °C after the LRS failure at 200 °C. The current levels and the set/reset voltages are about the same as before the LRS failure.

IV. CONCLUSION

In conclusion, the resistive switching behavior of the partially anodized aluminum thin film at elevated temperatures has been investigated. Both the $V_{\text{reset}}$ and $V_{\text{set}}$ decrease with increasing temperature, showing Arrhenius-like dependence with small activation energies. No large change in the set/reset voltage and the temperature dependence is observed after $10^4$ set/reset cycles. The pulse voltage experiment also suggests that the CF breaking/reconnection is easier to occur at a higher temperature. At elevated temperatures, while the HRS exhibits no significant change, the LRS shows a continuous degradation
with time, and there is an abrupt increase in its resistance. The LRS retention failure time shows Arrhenius dependence with an activation energy of \( \sim 1.3 \) eV, which suggests that the LRS failure could be due to the dissolution of some CFs caused by the migration of the excess Al atoms at high temperatures.

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