Preparation of Oxide Thin Films for Resistive Switching Memory by Plasma Assisted Pulsed Laser Deposition

S. Otsuka, T. Shimizu, S. Shingubara, S. Kurumi, K. Suzuki, T. Watanabe, Y. Takano, and K. Takase

Abstract—**We have investigated the reproducibility of current-voltage characteristics of resistive change random access memory (ReRAM) with the simple sandwiched structure of Al/Al_2O_3/Al whose insulating oxide film is deposited by a plasma assisted pulsed laser deposition (PAPLD) method, where three kinds of hydrogen, oxygen, argon plasmas were selected to change the film's quality. Three samples prepared by different additional plasmas show significant differences in the switching voltage reproducibility which is numerically evaluated by the ratio of the maximum switching voltage to the minimum (RMM). The hydrogen plasma treated sample shows good improvement of RMM.**

Index Terms—**ReRAM, pulsed laser deposition.**

I. Introduction

Successful development of a flash memory has provided many benefits in the memory storage. However current increment of the memory amount transferred at a time requires much faster response speed to the memories. Recently, several kinds of new memories based on new operating principles such as a phase change memory (PRAM) [1] and a magnetoresistive memory (MRAM) [2] have been proposed and extensively studied. One of new generation nonvolatile memories resistive change random access memory (ReRAM) also has attracted huge interests due to the faster response speed, simple structure, nonvolatility [3]-[5]. Many proposals about the combination of electrodes and insulators have been reported recently because the interesting switching phenomena are observed in the various insulators [6,]-[9].

For the practical use, the reproducibility of the switching voltage between metallic and insulating states is very important. However many kinds of devices show poor reproducibility [11]. The interesting switching phenomena might be understood in terms of the generation and breaking of conductive filament paths with different conductivity and the length made in the insulator at the soft breakdown [3]. According to the filament model, the variation of the switching voltages is thought to be caused by the random choice of the filament with different conductivity at every switching. For the suppression of the variation of switching voltages, the reductions of filament number and kinds are expected to be effective on the basis of this model.

In our previous works using anodic porous alumina as an insulator, we revealed that lowering the resistivity of the insulator, which made it easy to form the filaments with the same conductivity, by electrochemical treatments in electrolyte solutions improved the variation of the switching voltage [12]. The electrochemical treatment is a typical wet process. A dry process is more useful for device fabrication. In this study, a plasma assisted pulsed laser deposition (PAPLD) method as a dry process has been used for the insulating thin film growth. The added plasma is expected to change the film quality prepared by a usual PLD method, depending on the kinds of the gases. When choosing the oxygen plasma with chemical activity, it might provide excess oxygen atoms, which lead the deviation of the stoichiometric ratio, to the film. Such a nonstoichiometry lowers the resistivity. The hydrogen plasma as another chemically active plasma is expected to compensate the excess oxygen vacancies as originations for conductive filaments at the soft breakdown, thus the decrease of the filament number and kinds is perspective. Non-chemical active Ar plasma which provides the kinetic energy may introduce many vacancies. Aluminum oxides as insulating oxides were focused due to the stability against usual circumstances. The current-voltage (*I-V*) characteristics of the Al/Al_2O_3/Al capacitor whose insulators were prepared using the different kinds of plasma have been investigated and the reproducibility of the switching voltage has been evaluated.

II. Experimental

Figure 1 shows the schematic figure of the capacitor structure of Al/Al_2O_3/Al fabricated in this study. Firstly, the Al bottom electrode was evaporated on a quartz substrate using a conventional thermal deposition method. Figure 2 depicts the deposition system consisting of a pulsed laser ablation (PLD) system and an inductive coupled plasma (ICP) generator for the oxide insulator. Details of the ICP-PLD method are reported elsewhere [13]. Aluminum oxides were deposited in a steel chamber with the background pressure of 8.0×10^{-2} Torr using the Nb:YAG pulsed laser (LOTIS, LS2147, wavelength = 532 nm, laser energy = 30.0 mJ, pulse width = 20 nano-seconds, repetition frequency = 10 pulses per second), where the target is a high purity aluminum plate

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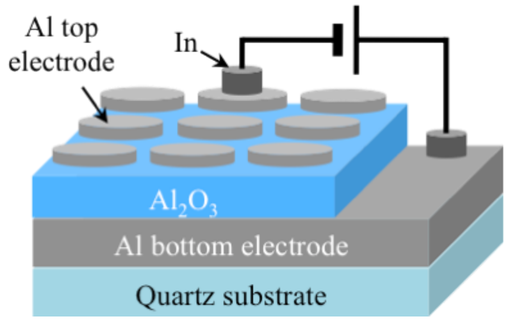

Fig. 1 Schematic structure of the capacitor of $Al/Al_2O_3/Al$

(99.999%) and the substrate temperature is room temperature. Any oxygen sources were not used because the residual gases in the low vacuum circumstance can easily oxidize aluminum ions evaporated by the PLD system. Three kinds of plasmas, Ar, O_2, H_2, produced by a radio frequency source (frequency = 13.56 MHz, incident power = 200 W) were irradiated to the ablation plume as shown in figure 2. Finally, Al thin film as the top electrode was formed by thermal deposition. The surface and the cross-section morphology were observed by scanning electron microscope (SEM). The *I-V* characteristics were examined from 0 V to 7 V by two-probe method at room temperature, where a mono-polar operation was adopted instead of an ordinary bi-polar operation. The upper limit of the current was set to 1 mA to guard the devices from complete dielectric breakdown by excessive currents. The reproducibility of switching voltages was evaluated through *I-V* characteristics measured a hundred cycles.

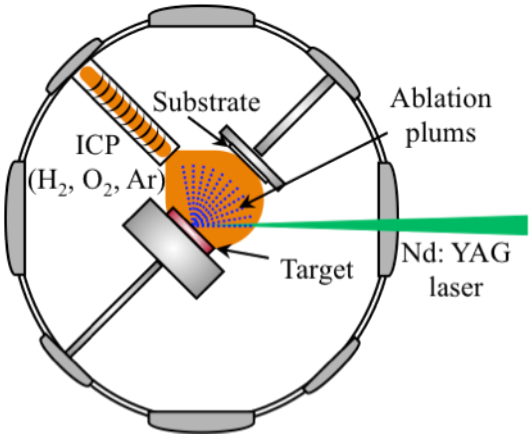

Fig. 2 Deposition system consisting of a pulsed laser ablation (PLD) system and an inductive coupled plasma (ICP) generator

III. Results and Discussion

Figure 3 shows the cross-section SEM image and the schematic view of the sample prepared by oxygen plasma. The thickness of the oxide thin film sandwiched by both electrodes is about 60 nm. Those of remaining two samples have almost the same values.

Figure 4 [(d) ~ (f)] shows the *I-V* characteristics, where the "SET" voltages are the thresholds at which the resistive

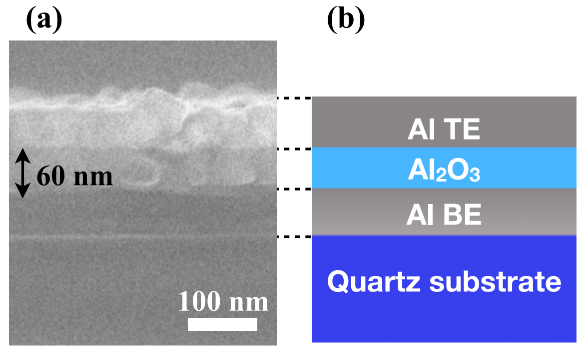

Fig. 3 Cross-section SEM image (a) and the schematic figure (b) of the sample prepared by oxygen plasma

changes from a high resistive state (HRS) to a low resistive state (LRS) and "RESET" voltages are the voltages for the opposite changes (LRS=>HRS). The device in a HRS as an initial state shows gradual increase of the current with increasing the applied voltage. When crossing the threshold voltages, the resistive state changes to a LRS which is kept in decreasing voltage down to zero. The second time applying the voltage causes a sudden descent of the currents, which means the return to the HRS, at the RESET voltage. All of the $Al/Al_2O_3/Al$ capacitors indicate mono-polar operation with the "window" of the *I-V* curves, whose open space means the reliability and the reproducibility of the devices. The Ar ICP treated sample shows the smallest window with the large leakage current in the HRS. The sample whose insulator was prepared by oxygen ICP, on the other hand, indicates the largest window. In case of hydrogen ICP, the leakage current of the HRS is relatively smaller than that of the oxygen ICP sample as the compensation was expected. The histograms are plotted to evaluate the reproducibility of the switching voltages in figure 4 [(a) ~ (c)]. The ratio of the maximum switching voltage to the minimum (RMM) is also calculated. The Ar sample has the wide and broad distribution for the SET voltages with the RMM of 5.4. The narrowest distribution with the RMM of 1.9 is observed for the oxygen sample. The hydrogen sample exhibits the broad and low distribution in the middle range of voltage and the narrow and high distribution in the higher voltage region.

Figure 5 shows the cycle number dependences of the SET and RESET switching voltages. The SET switching voltages of oxygen sample is the narrowest distribution in these three samples.

These results reveal that the ICP is quite effective on the *I-V* characteristics of the $Al/Al_2O_3/Al$ capacitors. The oxygen sample indicates the best result in these three samples, focusing on the RMM. It should be noted that the hydrogen sample has the good possibility to reduce the variation of the switching voltages because the RMM of the narrow distribution in the higher voltage region is 1.3, which is small enough for the practical application, with high incidence of 70 times among a hundred trials.

IV. Conclusions

The three capacitors of $Al/Al_2O_3/Al$ have been prepared by the PLD method assisted by three kinds of ICP (Ar, O_2, H_2) to evaluate the variation of the switching voltage. The

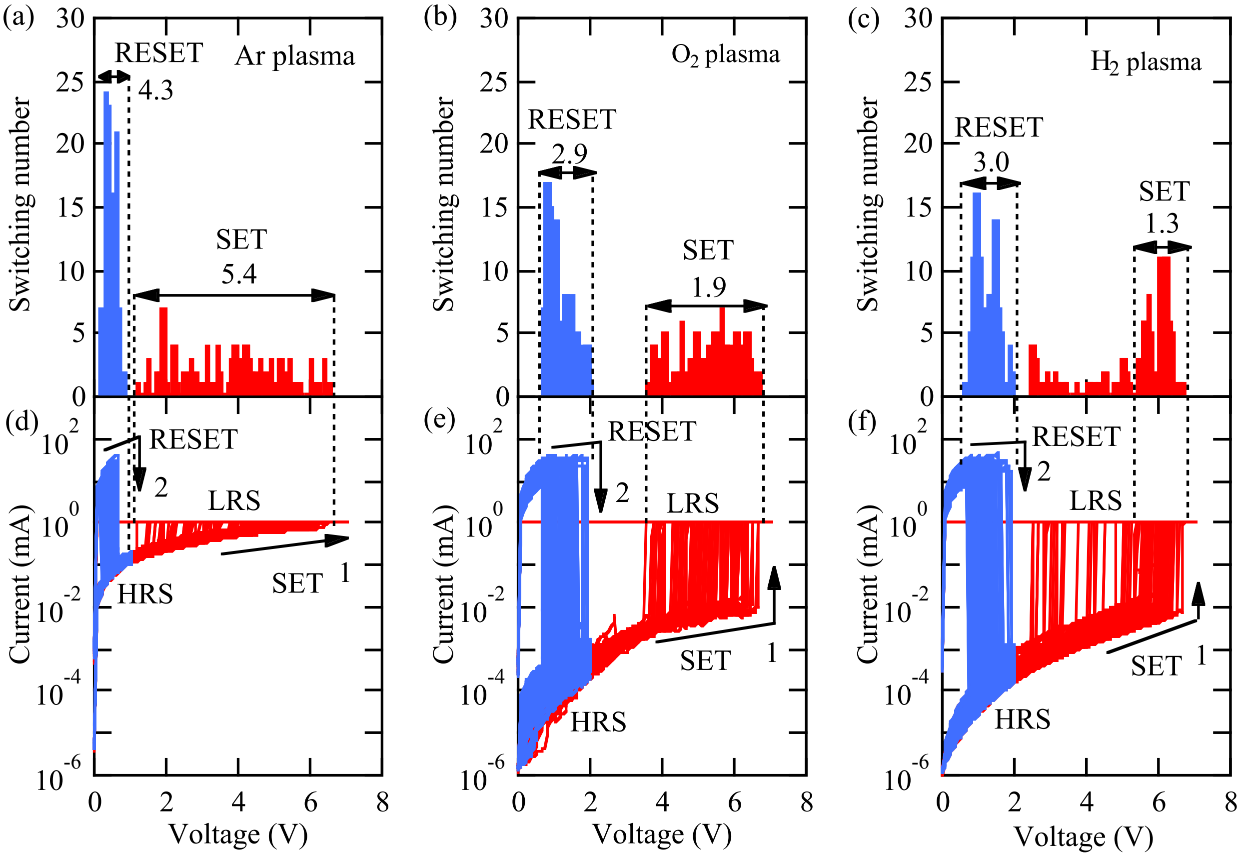

Fig.4 Histograms [(a) ~ (c)] of the switching voltages and the *I-V* characteristics [(d) ~ (f)] of three kinds of samples (Ar, O_2, H_2).

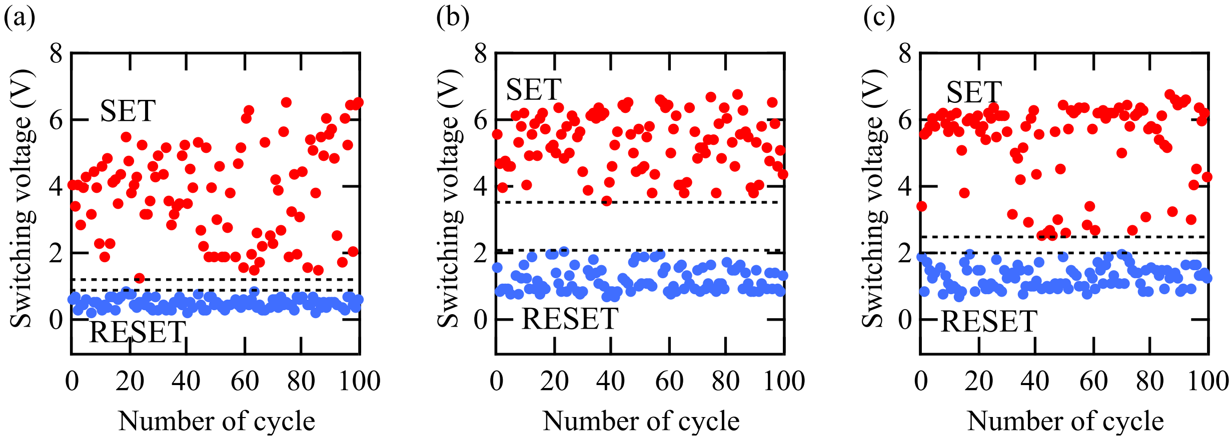

Fig.5 Switching voltage in the SET and RESET dependent on the number of cycles [(a) ~ (c)] of three kinds of samples (Ar, O_2, H_2).

oxygen sample shows relatively narrow distribution of the SET switching voltages with 1.9 RMM. The switching voltage spectrum of the hydrogen sample consists of the wide and low distribution and the narrow and high distribution with high incidence. These results imply that the added ICP is effective on the *I-V* characteristics the $Al/Al_2O_3/Al$ capacitors, especially for the variation of the switching voltage, as we expected.

Acknowledgment

This work is supported by the KAKENHI Grant Number 23310083 from Japan Society for the Promotion of Science (JSPS), and Strategic Project to Support the Formation of Research Bases at Private Universities: Matching Fund Subsidy from Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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ISBN: 978-988-19252-6-8
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

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