Fabrication of Tantalum Oxide Thin Film Using Wet Process and Study on Resistive Switching Memory

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ABSTRACT : *With the development of information society, the amount of data handled by human beings is rapidly increasing. Therefore, data storage media have been actively studied, especially resistive switching memories are attracting attention as next generation memory devices. The device has a very simple structure in which the resistance changing layer is sandwiched between upper and lower metal electrodes. In this research, we aimed to fabricate this resistance-change layer by wet process and demonstrate its operation as resistive switching memory. The wet process is low cost and suitable for mass production. Tantalum oxide was used as theresistance-changelayer, gold was used for the lower electrode, and aluminum was used for the upper electrode. As a result, it showed stable operation even when the ON/OFF ratio is about* 10^4 *and the retention characteristic is over 10,000 sec. This suggests the possibility of resistive switching memory by wet process.*

KEYWORDS –*Wet process, Resistive switching memory, Tantalum oxide*

I. INTRODUCTION

Large-capacity nonvolatile memories are used in many electronic devices around us, such as music players, cameras, and smartphones. The total amount of digital data produced by human continues to grow, including not only networks but also distributed save formats, and is expected to reach 44 ZB/year by 2020 [1]. In particular, a nonvolatile memory is used for distributed data save. Typical example thereof is NAND flush memories. NAND flush memories have increased capacity densities due to advances in technicals for miniaturizing semiconductor processes. Recently, the memory has reached the limit of miniaturization, and further high recording density has been promoted by changing the memory from a conventional two-dimensional type to a three-dimensional structure [2]. On the other hand, with a dramatic increase in the amount of information, an increase in power required for rewriting or reading data and a time required for accessing data have become issues. In view of these issues, R&D on new nonvolatile memories capable of operating at high speed and low power consumption has been actively conducted, and among them, ReRAM(Resistive Random access memory) has attracted attention as satisfying the requirements for high speed and low power consumption operation [3, 4, 5, 6, 7, 8]. MIM (Metal-Insulator-Metal) structures in which resistance-change layers are sandwiched between electrodes and a simple structure are being actively study and developed to increase the capacity.

In many studies of resistive switching memories, film formation is performed by a vacuum process. This is because it is necessary to strictly control the oxidation state of the metal oxide serving as the resistance change layer. However, in view of cost reduction due to a simple structure which is an advantage of the resistive switching memory, it is desired to fabricate the resistive switching memory by a simpler process. Therefore, this study demonstrates that an oxide layer is formed by a wet process and a device using the thin film can be sufficiently used as a resistive switching memory. Advantages of this method include that a large amount of substrates can be processed at a time, and that the film can be easily formed at room temperature and ambient pressure, so that the cost required for the equipment and chemicals can be suppressed to a low level. Tantalum oxide is used for the oxide layer. This is because it has already been reported as a resistive switching memory in many cases, and it is reliable as a material to be incorporated in a semiconductor process.

II. EXPERIMENTS

2.1 Solution making process

Precursor solutions were prepared by mixing $Ta(OC_2H_5)_5$ (high purity Scientific Lot. 4255921 purity 99.9%), CH_3COOH (Sigma Aldridge Lot. K8543), and C_2H_5OH (Sigma Aldridge Lot. M2580 purity 99.5%) [9].CH_3COOH (1 ml), C_2H_5OH(10 ml) was charged into the flasks, stirred for 10 minutes, and transferred to a separate container (solution 1). Similarly, CH_3COOH (1 ml), C_2H_5OH(30 ml) was charged, and after stirring for 10 minutes, nitrogen was replaced, $Ta(OC_2H_5)_5$ was injected, and the mixture was stirred for 30 minutes (solution 2). The Solution 1 was injected with a syringe and stirred for 18 hours to make precursor-solution. This solution was dropped onto a silicon substrate, spin-coated (3000 rpm,1 min), and annealed (500 °C to 800 °C) to prepare a thin film sample. XRD (X ray diffraction) and TDS (Thermal desorption spectrometry) of the produced tantalum oxide thin film were measured.

2.2 Fabrication process of the resistive switching memory

A Si substrate with an Au/Cr film was prepared by vapor deposition. The contact portion of the lower electrode was protected with Kapton tape. Precursor solution was added dropwise, 3000 rpm,1 min was performed by spincoating, and vacuum-drawn in a desiccator to dry the precursors. Next, annealing at 600 °C was performed in an electrical furnace. A top electrode (Al) was formed by resistance heating evaporation using a metal mask having an open circular pattern. The sample structure is shown in FIG. 1.

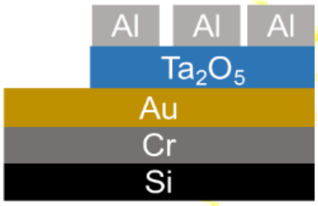

FIG. 1 The structural drawing of the fabricated tantalum oxide resistive switching memory.

III. RESULTS AND DISCUSSION

3.1 Evaluation of tantalum oxide thin films

TDS was used to assess the gas evolved during the calcination of pre-calcined samples made using precursor solutions. The results are shown in FIG. 2. It was found that H_2O was desorbed in the temperature range of 50 °C to 600 °C. A strong peak occurs again at 300 °C to 450 °C, and this is considered to be due to dehydration condensation occurring inside the film by heating. In addition, it was confirmed that the organic matter was desorbed at 200 °C to 500 °C After that, it is considered that all the reactions were completed and the Ta_2O_5 film could be formed.

When the tantalum oxide thin film produced in FIG. 3 was fired at 700 °C or higher in four patterns of 500 °C, 600 °C, 700 °C, and 800 °C showing the measurement results by XRD, peaks were observed at 22 °, 28 °, 37 °, and 47 °. It can be inferred that tantalum oxide crystallized at 700 °C is obtained and an amorphous tantalum oxide thin film is obtained at 600 °C since the generation point and the peak-to-peak ratio are identical with those of the β-layer of the Ta_2O_5.

From the XRD measurement results and the TDS measurement results, it is considered that annealing at 600 °C is optimal for obtaining an amorphous tantalum oxide thin film with few impurities in the film. The grain boundaries generated when crystallization occurs are undesirable because they cause leakage. Therefore, a tantalum oxide layer fabricated at 600 °C is used for fabricating the resistive switching memory.

3.2 Band analysis of resistive switching memory

PYS (Photoelectron yield spectroscopy) measurements were performed to infer the banding structures of the fabricated devices. FIG. 4 shows the results of PYS measurement of each material (Au, Al, Ta_2O_5) used for device fabrication. Although the idealized values of the work functions of Au used for the lower electrodes are 4.7 eV, the results of measurements in this study are 4.7 eV. Although the ideal value of the work function of Al used for the top electrodes is 4.13 eV, the value measurement in this laboratory was 4.2eV.The Ta_2O_5 used for the oxide layers has no difference in thresholds due to the difference in annealing condition, and is 5.0 eV. Based on these results, a band diagram as shown in FIG. 5 is shown. The bandgap of Ta_2O_5 has been reported to be 4.0 eV [10]. Since the Fermi level exists in the central of the band gap when the insulator is ideally used, it is considered that there is a barrier of 1.7 eV at the Au/ Ta_2O_5 interface and a barrier of 1.2 eV at the Al/ Ta_2O_5 interface. Therefore, it is considered that the device in the initial state exhibits insulating properties.

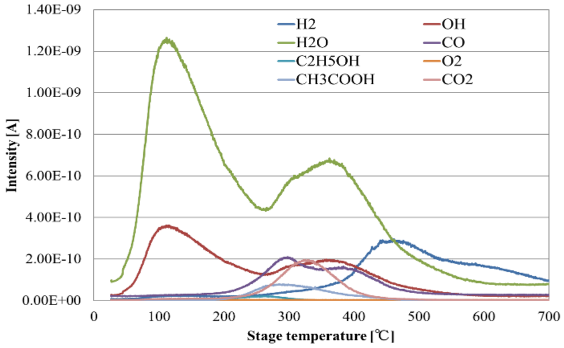

Fig. 2 TDS measurement results of the tantalum oxide thin film produced by the solution

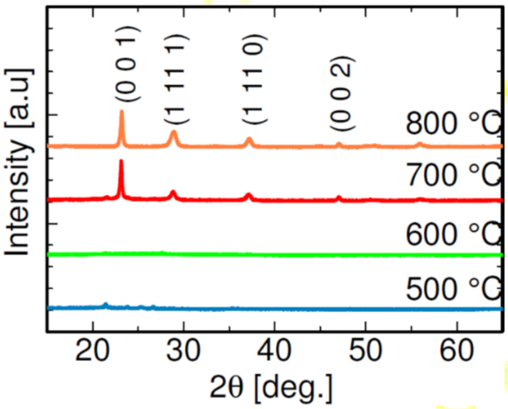

Fig. 3 XRD characteristics of tantalum oxide thin film when annealed at changing temperature

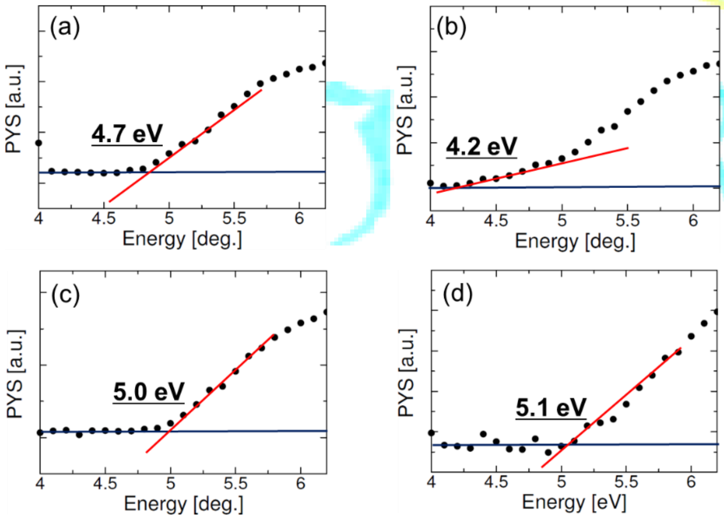

FIG. 4 The PYS-measurement results of the respective layers (a: Au, b; Al, c; Ta_2O_5_600 °C, d; Ta_2O_5_700 °C) of the resistive switching device.

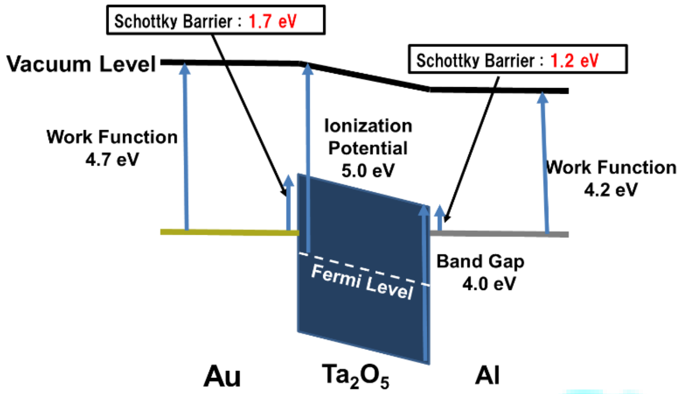

FIG. 5 Estimated band-structure diagram based on the PYS results.

3.3 Evaluation of memory characteristics

The I-V characteristics of the fabricated devices were measured using a manual prober and a semi-semiconductor parameter analyzer (Keysight 4145B). The dielectric breakdown of the device was controlled for the 10 mA of limiting the current at positive biases. The top electrode formed of Al was used as an anode, and after a voltage was applied from 0 V to +10 V, a voltage was applied in the opposite direction to − 5 V, and the electrode was returned to the 0 V. Fig. 6 shows these results. On the plot, the current rises rapidly in the + 6.6 V. Here, it is considered that a conductive path is formed between the electrodes and a low resistance state is obtained. When voltages were applied from the + 10 V to the 0 V, the current values showed high conductivity. Subsequently, when the voltage was applied in the opposite direction, the current value decreased at the point where the voltage reached the negative 2 V. Here, it is considered that the device was switched to a high-resistance condition by anodization, and the current values showed insulating properties when voltages were applied from − 5 V to 0 V.

FIG. 7 shows the results of the I-V characteristics when the current limit is changed from 1 mA to 5 mA to 10 mA. As the limitation of the current increases, the current values at the time of Reset tend to increase. This is believed to be due to the fact that the diameter of the conductive filaments spreads as the current limit increases, affecting the Reset operation.

In addition, the endurance characteristics (repetition resistance characteristics) were measured when the current limit was set to 10 mA at positive biases. The results are shown in FIG. 8. In the same manner as in FIG. 6, a change operation was performed, and the current values at the applied-voltage 0.5 V were evaluated. It can be seen that the ON/OFF ratio varies greatly by a factor of 10^4. Further, the characteristics are almost unchanged even after 10 repetitions. In the resistive switching memory, a change of about four orders of magnitude is sufficient, and this is the result of this research.

FIG. 9 shows retention-time characteristics. After changing to the low-resistance state, an applied-voltage 0.5 V equal to or lower than the threshold value was applied to measure the current value in the ON state at intervals of time. The resistance was changed to the high resistance state, and the current value in the OFF state was evaluated in the same manner. In both the ON state and the OFF state, very stable characteristics were exhibited at about 10,000 sec.

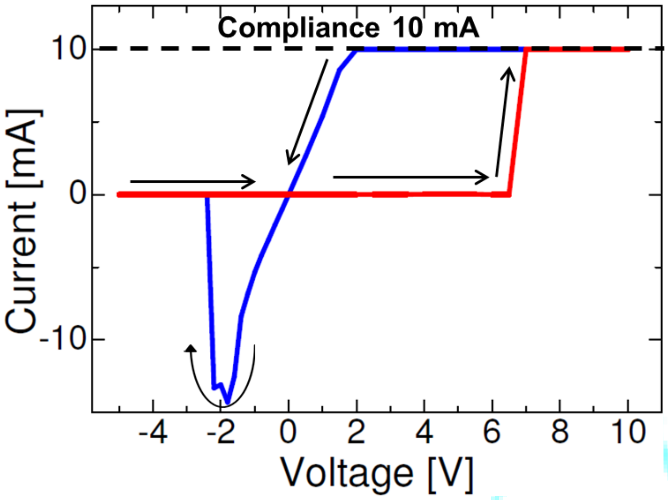

Fig. 6 I-V characteristics (current limiting 10 mA) of thefabricated resistive switching memory

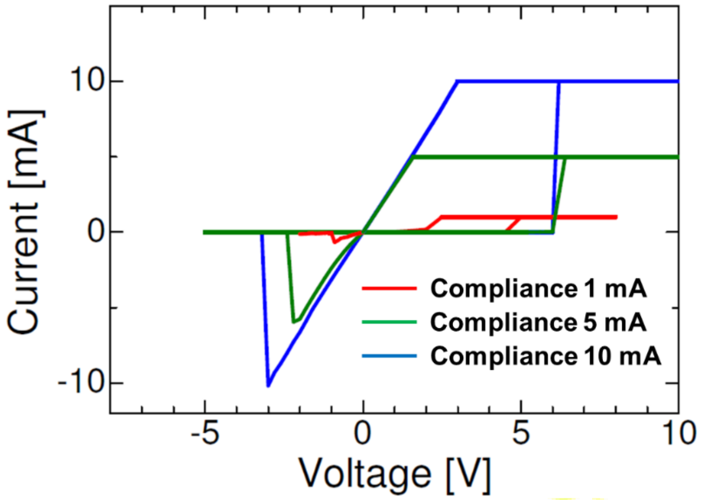

Fig. 7 I-V Characteristicsof thefabricated resistive switching memory due to changes in current limit values (compliance)

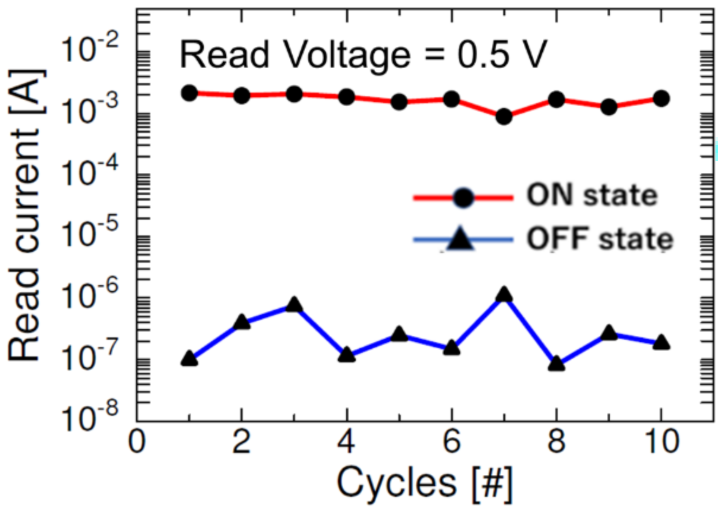

FIG. 8 Endurance characteristics of thefabricated resistive switching memory

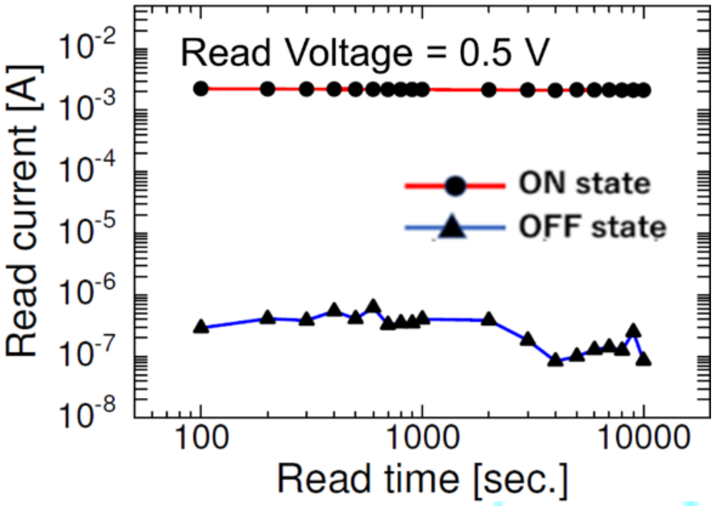

Fig. 9 Retention-time characteristics of the fabricated resistive switching memory

IV. CONCLUDION

In this study, the resistive switching memory was simply fabricated by a wet process and the memorycharacteristics was evaluated.As a result of evaluating the crystallinity of tantalum oxide, a strong peak of Ta_2O_5 was observed in the sample calcined at 700°C, whereas no peak was observed in the sample calcined at 600°C. In addition, it was confirmed from the experimental results using the temperature raising desorption method that H_2O was desorbed at 50°C to 600°C, CO was desorbed at 200°C to 500°C, and O_2 was desorbed at 250°C to 400°C. From these results, it is considered that annealing at about 600°C is appropriate to obtain amorphous tantalum oxide. By measurement the I-V characteristics of the fabricated resistive switching memory and evaluating the endurance characteristics and the retention-time characteristics, it was possible to confirm the switching operation of the low resistance state and the high resistance state, and the demonstration of the operation was successful. These stable resistance change operations suggest the possibility of a resistance change device by a wet process.

V. ACKNOWLEDGMENTS

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