Low-Frequency-Noise Spectroscopy of TaO\(_x\)-based Resistive Switching Memory

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Research and development into resistive switching memories, such as resistive random access memory (ReRAM) and memristors, are being actively promoted toward the realization of new computing techniques. To improve the reliability of these devices, it is important to clarify their resistance characteristics. Low-frequency-noise spectroscopy (LFNS) is a powerful method for investigating the nature of traps in conduction paths, even at the nanoscale. In this article, the results of LFNS measurements on a TaO\(_x\)-based ReRAM device are presented. The temperature dependence of the noise spectra at given frequencies reveals the existence of multiple trap levels, which are observed over a wide range of resistance values. These experimental results show that the ReRAM device is particularly advantageous when used in analog resistive switching applications.

1. Introduction

To realize a human-friendly cyber-physical system, it is essential to reduce the size and power consumption of edge IoT devices.[10] IoT devices that can be driven without a power supply are desired, for example, devices that can run only using energy harvesting technologies.[11] This requires a fast, low-powered, and highly integrated non-volatile memory. Resistive switching memory, such as resistive random access memory (ReRAM), has considerable potential for these types of applications.[3–6]

ReRAM has a simple structure in which the oxide layer is sandwiched between metal electrodes. The fundamental mechanism for the transition between the high-resistive state (HRS) and low-resistive state (LRS) in ReRAM cells is the nanoscale redox reaction involving oxygen ion migration.[7–15]

Reactions are observed in various oxides that can be handled in a process compatible with existing semiconductor technologies, which support the practical application and commercialization of ReRAM.[16] One of the advantages of resistance changes in ReRAM is the high resistance change ratio, and it is possible to control the resistance change in an analog manner.[17–19] Such devices are called memristors or resistive analog neuromorphic devices (RANDs), which are being actively studied for realizing various emerging computing techniques such as neuromorphic computing, reinforcement learning, and reservoir computing.[20–26]

Although excellent non-volatile and dynamic performances have been reported in both digital and analog resistive switching operations, the nature of resistance switching should be evaluated in detail for further improving the reliability, particularly in nanoscale devices. The random variations in device characteristics have emerged as a crucial issue. A possible reason is the read current fluctuation associated with random telegraph noise (RTN). On the other hand, because RTN signals are due to the trapping/de-trapping of mobile carriers in the current path of a device, noise spectroscopy can be applied to investigate the conduction mechanisms quantitatively.[27,28]

In fact, low-frequency noise is essentially generated by crystal imperfections, and noise measurements have been used to investigate defects. The analysis of low-frequency noise showed that power spectral density was approximately proportional to \(1/f\) for the conventional operation mode of HfO\(_2\)-based ReRAM, while that of HRS was clearly proportional to \(1/f^2\) when a limited number of traps resulted in the characteristic of HRS.[29] A factorial hidden Markov model was used to solve the statistical properties of each trap contributing to multi-level RTN in HfO\(_2\)-based ReRAM.[30] The complex RTN was separated in multiple 2-levels RTN. Previous studies of the low-frequency noise analyses also revealed that the conductive filaments existed in LRS, the filament was ruptured, and the tunneling gap was formed during the reset process.[31–34] Low-frequency noise spectroscopy (LFNS) is a powerful method for determining the nature of traps in field-effect transistors (FETs).[35,36] Energy levels were derived from the noise spectra obtained at different temperatures. Since the conduction path can be evaluated quantitatively even at the nanoscale, LFNS studies have been conducted on gate-all-around nanowire FETs.[37] In this study, LFNS measurements were performed to investigate the origin of the resistance change in a ReRAM device over a wide temperature range from...
low temperature to room temperature. The temperature dependence of the noise spectra at given frequencies revealed that multiple trap levels exist and that they are related to the electrical resistance of the device.

2. Results and Discussion

LFNS measurements were performed on a resistive switching device with an identical TiN/TaOx-L/TaOx-H/TiN structure. The device with the TaOx-L-TaOx-H stacking structure showed excellent characteristics for the low-power neural-network processor. The resistance states were adjusted at low temperatures before the LFNS measurements. Three resistance states were prepared, with resistance values of 11 MΩ, 455 kΩ, and 6 kΩ, as shown in Figure 1. Notably, the resistance intervals were set to be sufficiently large provided that the deterioration of the device does not occur. Hereinafter, we describe them as high-, medium-, and low-resistance states, denoted by HRS, MRS, and LRS, respectively. A noise analysis was performed based on previous studies. The capture time (τ) for an electron trap can be expressed as:

\[
\tau = \exp\left(\frac{E_A}{k_B T}\right) \left(n, v, \alpha_t\right) \quad (1)
\]

where \(E_A\) is the activation energy for the trap state, and \(k_B\) is the Boltzmann constant. \(n, v, \alpha_t\) are the electron density, electron thermal velocity, and capture cross-section, respectively, assuming that the emission time from the electron trap is equal to τ. By focusing on the given frequencies (f) and peak temperatures, the activation energy \(E_A\) can be evaluated using the following equation:

\[
\ln(T^{0.5} f) = \left(\frac{E_A}{k_B T}\right) + \text{Const.} \quad (2)
\]

where the effective density of the band states is assumed to be less temperature-dependent. Even if it is calculated as being temperature-dependent, \(T^{0.5}\) is replaced by \(T^2\) in Equation (2), and it was confirmed that the change in the activation energy value was 20% or less. The discussion in this study was unaffected by the temperature index. It is noted that Equation (2) with the \(T^2\) temperature-dependency, owing to the temperature-dependent density of states, is used for the determination of the nature of traps in semiconductor FETs.

Figure 2 shows the temperature dependence of the noise spectra of the three states. The spectrum intensities were normalized using the current. In the higher-resistance state, the normalized intensity increases. This tendency is commonly observed in Al/AlOx/WOx/W and TiN/Ti/HfO2/TiN structures. For peak fitting, spectra intensities without normalization are shown in Figure 3 as a function of the temperature. Figure 3a shows the temperature dependence of the LFNS for HRS. There are four distinctive peaks, namely HP1, HP2, HP3, and HP4, and their Arrhenius plots are shown in Figure 4a. By using Equation 2, the \(E_A\) values of these peaks were estimated to be 29, 132, 287, and 439 meV, respectively. Figures 3b and 4b show the temperature dependence of LFNS and the Arrhenius plots for MRS, and those for LRS are shown in Figures 3c and 4c, respectively. The LFNS analysis results for all the three resistance states are summarized in Table 1. For the sake of discussion, the results are classified into three groups based on the magnitude of the activation energy. Although the activation energy of oxygen diffusion has been studied quantitatively, the conductance mechanism of the electrons in resistive switching devices has not been fully investigated. As described below, the defect states with the activation energy above 300 meV (Group III) were experimentally observed, while those below 100 meV (Group I) have not previously been experimentally reported on Ta oxide-based devices to our best knowledge. The defect state with an activation energy of 0.8 eV, assigned to the first ionization level of the O vacancy deep double donor, was experimentally detected in Ta2O5 capacitors with an ultrathin film thickness using zero-bias thermally stimulated current spectroscopy (ZB-TSC). ZB-TSC also
exhibited activation energies of 0.2, 0.3, 0.4, and 0.49–0.57 eV, due to the vacancy complex shallow single donor in slightly different configurations. The Poole–Frenkel effect was observed at the trap level with a lower activation energy, and the trap was assigned as an oxygen vacancy.\textsuperscript{[39,43]} Photocurrent measurements revealed an activation energy of 0.25 eV in a tantalum oxide film prepared by reactive sputtering.\textsuperscript{[43]} From these investigations, it is reasonably considered that the origin of the traps in Groups II and III is oxygen-vacancy related. The origin of the traps with an activation energy of < 100 meV is unclear; however, an energy of 39 meV has been reported for AlO\textsubscript{x}/WO\textsubscript{y} resistive switching devices. Because the peaks in Group I became evident in the LRS, the trap states with the lower activation energy are considered to originate from the LRS of the device. Notably, the theoretical calculations based on the local density approximation showed that the band width of the oxygen vacancy was as wide as 1.0 eV in Ta\textsubscript{2}O\textsubscript{5}.\textsuperscript{[44]} This indicates that the vacancy states interact with each other and that the distorted local structures around the oxygen vacancies can have a strong impact on the interactions.

We emphasize that all the trap states, Groups I, II, and III, were observed in the three resistance states. The device resistance varied from 6 kΩ to 11 MΩ, which was more than three orders of magnitude. This provides a conductance model of resistance switching with traps as the noise source. Figure 5 illustrates the filament conduction in the resistive switching device. The TaO\textsubscript{x}-L layer acts as the supplier and reservoir of the oxygen vacancies which are the sources of electron traps. The color of this layer is light blue because it contains many oxygen vacancies. The resistance of the device is determined by that of the TaO\textsubscript{x}-H layer, and the isolated vacancy, indicated by the red circle in the figure, is considered to be the origin of electron trapping/de-trapping in the insulator-like resistive layer. The resistance transition to LRS is brought about by the application of a positive voltage, as shown in Figure 1. The oxygen movement to the upper TaO\textsubscript{x}-L reservoir layer leads to the increase of oxygen vacancies in the bottom TaO\textsubscript{x}-H layer and the resistance transition to LRS. In the negative voltage sweep, the oxygen vacancies in the TaO\textsubscript{x}-H layer decrease, with more oxygen moving back to the bottom TaO\textsubscript{x}-H layer under the higher current, leading to a resistance transition to MRS and HRS. Because the trapping/de-trapping of the electrons were observed even in the LRS as shown in Figure 3c, the traps are considered to be located not only inside the resistive switching conductance path but also around the path.\textsuperscript{[40]} A reliability model of the digital and analog resistive switching of ReRAM was proposed, and the encapsulated cell, in which the sidewall was protected, showed better device performance.\textsuperscript{[45,46]} Considering our model, we can conclude that as the size of the device is reduced, it becomes critical to suppress the oxygen vacancies that form around the conduction path. For example, in a miniaturized device that does not consider the sidewall, the fluctuation of resistance change becomes remarkable.

3. Conclusions

In conclusion, this study performed LFNS of a ReRAM device with a TiN/TaO\textsubscript{x}-L/TaO\textsubscript{x}-H/TiN stacking structure. We investigated the temperature dependence of the LFNS and evaluated the activation energies of the trap states. The higher the device
resistance, the higher the intensity of the noise power spectra. Based on the activation energy, we classified these traps into three groups. The three trap groups were observed at all device resistance values, as opposed to the spectral intensity, which depended on the device resistance. The trap process is significantly involved in the electrical conduction of the device, even in the low-resistance state. The present study demonstrated that traps with various energy depths contributed to electrical conduction over a wide range of resistance values of the ReRAM device. This fact is expected to play an advantageous role in controlling analog resistance of the device, because the existence of traps having various energy depths facilitates continuous changes in resistance value. Although the neural algorithm is generally robust against noise during operation, the noise may cause asymmetric nonlinearities in the analog resistance, which reduces the accuracy.\textsuperscript{[47]}

Although the standard methods to evaluate the trap energy quantitatively, such as TSC and Deep Level Transient Spectroscopy, require a sample with a large enough interface area to detect the signal, LFNS measurements enable us to investigate the trap even in the nanowire-shape device; hence, it can be expected to contribute to solving these problems by evaluating state-of-the-art devices at the level used in products on the market.

Table 1. Activation energies obtained from the Arrhenius plots. The peak numbers shown in Figures 3 and 4 are also presented. For the sake of discussion, the results are classified into three groups based on the magnitude of the activation energy.

| Resistive state | Group I [<100 meV] | Group II [100–300 meV] | Group III [>300 meV] |
|-----------------|-------------------|------------------------|---------------------|
| HRS             | HP1 29            | HP2 132                | HP3 287 HP4 439     |
| MRS             | MP1 44            | MP2 276                | MP3 486 MP4 539     |
| LRS             | LP1 31            | LP2 56                 | LP3 91 LP4 203 LP5 314 |

Figure 4. Arrhenius plots using peak temperatures for a) HRS, b) MRS, and c) LRS.
photolithography and dry-etching processes using a Cl2–Ar gas mixture. The thin film was patterned as the bottom electrode (BE) with conventional photolithography and dry-etching processes using a Cl2–Ar gas mixture followed by a chemical vapor deposition (CVD) process at 623 K (350 °C) to deposit a 30 nm-thick SiO2 layer, which conformally covered the TiN BE patterns. A via hole structure with a diameter of 300 nm was prepared by electron beam lithography and ion-beam etching using CF4 gas. After the ion-beam etching process, the TiN BE surface was exposed at the bottom of the via hole. Subsequently, a TiN top electrode (TE)/TaOx-L/TaOx-H/TiN BE stack structure was reactive-sputter-deposited on the TiN BE. Here, TaOx-L and TaOx-H represent the tantalum oxide layers prepared by RF reactive sputtering, which have different resistivity values. More specifically, the resistivity of TaOx-L was approximately 3 Ω cm, whereas that of TaOx-H exceeded 10 000 Ω cm.

4. Experimental Section

A 20 nm-thick TiN thin film was prepared by DC reactive sputtering on a thermally oxidized Si substrate. The reactive sputtering process for TiN was conducted in an Ar–N2 gas mixture with an Ar/N2 flow rate ratio of 7.0 SCCM/3.0 SCCM. The working pressure was approximately 0.065 Pa. The DC power during the sputtering process was maintained at 200 W. No substrate heating was performed. Subsequently, the TiN thin film was patterned as the bottom electrode (BE) with conventional photolithography and dry-etching processes using a Cl2–Ar gas mixture followed by a chemical vapor deposition (CVD) process at 623 K (350 °C) to deposit a 30 nm-thick SiO2 layer, which conformally covered the TiN BE patterns. A via hole structure with a diameter of 300 nm was prepared by electron beam lithography and ion-beam etching using CF4 gas. After the ion-beam etching process, the TiN BE surface was exposed at the bottom of the via hole. Subsequently, a TiN top electrode (TE)/TaOx-L/TaOx-H/TiN BE stack structure was reactive-sputter-deposited on the TiN BE. Here, TaOx-L and TaOx-H represent the tantalum oxide layers prepared by RF reactive sputtering, which have different resistivity values. More specifically, the resistivity of TaOx-L was approximately 3 Ω cm, whereas that of TaOx-H exceeded 10 000 Ω cm. The resistivity values were controlled by varying the Ar/O2 flow rate ratio during the reactive sputtering process. The RF power was maintained at 50 W. The thicknesses of the TiN TE, TaOx-L, and TaOx-H were adjusted to 60, 30, and 30 nm, respectively, for better analog-resistance controllability. By patterning the track structure, TiN TE/TaOx-L/TaOx-H/TiN BE devices with a diameter of 300 nm were prepared.

The DC electrical properties of the resistive switching devices were investigated using a Keysight B1500 semiconductor parameter analyzer. In the measurement of DC I–V curves, the integration time of each measurement point was automatically adjusted. As shown in Figure 1, LRS was realized by the positive voltage sweep with the current compliance. An external voltage was applied to the TE with the grounded BE. The LFNS measurement was conducted in a low-temperature cryostat, in which the device temperature could be precisely controlled in a He atmosphere within a temperature range of approximately 3–310 K. To detect the noise signal from the device, the current measurement system in the Keysight B1530A WFGMU was utilized. The applied voltage in the LFNS measurement was fixed at 0.1 V. It has been experimentally confirmed that the LFNS peak does not appear in the absence of the TaOx layer.

Conflict of Interest

The authors declare no conflict of interest.
