Impact of Film Morphology on the Switching Characteristics of Ta₂O₅-Based Atomic Switches

Cedric Mannequin¹, Tohru Tsuruoka¹, Tsuyoshi Hasegawa² and Masakazu Aono¹

¹ NIMS

International Center for Materials Nanoarchitectonics (MANA) 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan E-mail: MANNEQUIN.Cedricromuald@nims.go.jp ² Waseda Univ. Department of Applied Physics 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Abstract

The impacts of the oxide film density on the resistive switching characteristics of a Cu/Ta_2O_5 -based atomic switch were investigated. A lower film density induces a reduction in the operation voltages under atmospheric conditions. This is attributed to an increase of dangling Ta-O bonds that can form a hydrogen-bond network, providing migration paths for Cu ions. The results suggest the critical role of the film morphology of the matrix oxide in resistive switching behavior.

1. Introduction

The on-going downscaling of Si-based Flash memory has reached a physical limit, which is difficult to overcome. Resistive switching memory based on cation migration in a thin oxide film is considered as a good candidate for next generation, non-volatile memory applications, thanks to their promising properties such as their high density, high speed, low power consumption, low fabrication cost, and Back-End-Of-Line (BEOL) compatibility with CMOS technologies, ensured by a basic Metal/Insulator/Metal (MIM) structure [1]. Because of its similarity to the operating mechanism of 'gap-type atomic switch' [2], we refer to cation-migration-based MIM cells as 'gapless-type atomic switch' [3]. Recently, Tsuruoka et al. reported the effects of moisture on the operation of oxide-based atomic switches [4]. Here, we present how the oxide film morphology affects the switching behavior, in relation to moisture absorption from the ambient surroundings.

2. Experiments

Cross-point structured Cu/Ta₂O₅/Pt cells with a junction size of 5 μ m were fabricated on a Si substrate covered with SiO₂. Ta₂O₅ films were prepared by different deposition methods (RF sputtering (SP) and electron-beam (EB) deposition) in order to change the film morphology. The Cu and Pt electrodes were deposited by EB deposition. The deposited films were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy in Attenuated Total Reflectance mode (FT-IR-ATR), X-ray reflectometry (XRR), and X-ray photoelecron spectroscopy (XPS). The surface topography of the films was measured by atomic force microscopy (AFM). Current-voltage (I-V) curves were measured while alternating the ambient pressure condition as atmosphere – vacuum – atmosphere - vacuum. A bias voltage was applied to the Cu electrode and the Pt electrode was electrically grounded in all of the measurements. The cells showed bipolar switching behavior: SET from a high-resistance (OFF) state to a low-resistance (ON) state under positive bias to the Cu electrode, and RESET from the ON state to the OFF state under negative bias. From the measured I-V curves, switching parameters such as the forming (the first SET), forming-OFF (the first RE-SET), SET/RESET voltages, and ON/OFF resistances were evaluated.

3. Results and Discussion

The deposited Ta_2O_5 films were amorphous for both deposition processes, as confirmed by XRD and FT-IR-ATR. FT-IR-ATR spectra displayed a doublet peak in the 700-900 cm⁻¹ range, as shown in Fig. 1. This doublet is characteristic of the stretching mode of Ta-O-Ta bonds in an amorphous state. The slight deviation in the doublet position for EB and SP films indicates a change in the vicinity of the Ta-O bonds. Moreover, a higher intensity is exhibited in the 3600 cm⁻¹ region for EB films, indicating a more substantial amount of absorbed water than in SP films. XRR measurements showed that the EB film had a lower density (6.8 g/cm³) than the SP film (7.6 g/cm³), indicating higher porosity. XPS measurements indicated a higher amount of tantalum sub-oxide (not shown here).

Fig. 2 shows the variation of the SET and RESET voltages with changes in ambient pressure. The SET process corresponds to the formation of a Cu filament by inhomogeneous nucleation, while the RESET process was attributed to the dissolution of the filament due to oxidation of Cu assisted by Joule heating [5]. The cell with the SP film (SP-cell) exhibited almost constant operation voltages regardless of the ambient pressure, as indicated by the red circles. In contrast, the SET and RESET voltages of the cell with the EB film (EB-cell) increased in magnitude, when the atmosphere was evacuated, as shown by the blue squares. Other switching parameters such as the forming/forming-OFF voltages and ON/OFF resistances also exhibited a similar tendency (not shown here).



Fig. 1 FT-IR ATR Spectra of Ta₂O₅/ Pt stacks.

Fig. 3 represents variations of the OFF state current in different ambient conditions, measured before the forming. In the range of 3 - 4 V, the current exhibits a linear increase in a semi-log representation for both types of samples. In case of the SP-cell, the current is independent of the chosen atmospheric condition (filled and empty circles). In contrast, the EB-cell exhibits a strong dependence on the ambient pressure. The current slope of the EB-cell (empty squares: 1.39) indicates a similar tendency to the SP-cell in vacuum, but it increased drastically up to 3.42 (filled squares) in air.

As the switching parameters of the EB-cell in vacuum are almost identical to those of the SP-cell, an additional mechanism must be involved in the EB-cell to reduce the operation voltages in air. The lower density of the EB film, along with a high density of tantalum sub-oxide (evidenced by XPS analysis) favors the formation of hydroxylated tantalum oxide (Ta-OH) during air exposure. This, in return, allows the chemisorption of water, leading to the formation of a highly structured H₂O network in the oxide layer [6]. The consequence of moisture absorption on the switching properties is considered to be twofold. First, the presence of water favors the copper dissolution at the anode by enhancing the yield of the copper oxidation reaction [7]. Second, the Cu ions are trapped by hydrogen bonds within the structured H₂O network thus migrating within it, following an ionic hopping mechanism [1], leading to the current increase, noted in Fig. 3. Thus, the residual water enhances the creation and migration of Cu ions, giving rise to a decrease in the operation voltages in air. Under vacuum, the H₂O network partially vanishes, because a portion of residual water easily desorbs from the film. This drastically reduces the number of available Cu ions (lower rate of copper dissolution) and trapping sites (lower diffusivity) leading to an increase of the operation voltages. In case of the SP-cell, the higher film density reduces the amount of Ta-OH groups within the layer, preventing the formation of a H₂O network. The Poole-Frenkel contribution of the OFF state current masks the ionic current (low intensity) and operational voltages are increased to ensure Cu ions migration. Upon vacuum, this situation stays unchanged.



Fig. 2 SET and RESET voltages of Cu/ Ta₂O₅/Pt cells for different ambient pressures.



Fig. 3 OFF state currents before forming for EB- and SP-cells.

4. Conclusions

We have investigated the resistive switching characteristics of Cu/Ta₂O₅/Pt atomic switch cells with different Ta₂O₅ film morphology. It was found that a lower film density induces a reduction in the operation voltages under atmospheric conditions by enhancing moisture absorption. Our results indicate the importance of the film morphology of the matrix oxide in controlling resistive switching behavior.

Acknowledgements

This work was supported in part by CREST, Japan Science and Technology Agency (JST) and by JSPS KAKENHI Grant Number 24350278.

References

- [1] I. Valov et al., Nanotechnology 22 (2011) 254003.
- [2] K. Terabe et al., Nature 433 (2005) 47.
- [3] T. Hasegawa et al., MRS Bull. 34 (2009) 929.
- [4] T. Tsuruoka, et al., Adv. Funct. Mater. 22 (2012) 70.
- [5] T. Tsuruoka et al., Nanotechnology 21 (2010) 425205.
- [6] S. Trasatti et al., Elsevier (1981).
- [7] T. Tsuruoka et al., Adv. Funct. Mater (in press).