Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp140-141

Evaluation of the WO_X Film Properties for ReRAM Application

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Abstract

The formation condition, microstructure, and growth kinetics of the WO_X layer for WO_X ReRAM are investigated. To understand the optimal condition for the rapid thermal oxidation process which forms the WO_X layer, various annealing temperature and annealing time are systemically studied through TEM, XRD, Raman spectra analyses and electrical characterizations. The growth kinetics for WO_X under RTO is found similar to the one for thermal oxidation on silicon. The electrical forming voltages of the WO_X cells are also found independent from the oxide thickness, which further suggests the switching behavior of WO_X ReRAM takes place at the interface but not the bulk.

Introduction

The resistive switching memory (ReRAM) has attracted lots of attention as a promising candidate for the next generation nonvolatile memory aiming for high-density memory applications [1] for its simple MIM (metal-insulator-metal) structure, small cell size, high speed, low power consumption, and potential for 3-D stacking. In particular, the tungsten oxide (WO_X) ReRAM [2] possesses excellent electrical properties and is CMOS process compatible. In this work, through evaluating the oxidation temperature and oxidation time, not only the optimized process window is found but the oxidation mechanism and electrical properties are examined as well.

Device Fabrication

The WO_X ReRAM devices were fabricated following a standard back-end-of-line (BEOL) process [2]. After the metal lines were patterned as the bottom electrodes, W-plugs with standard via process at 0.24µm diameter were fabricated. The W-plugs were then subjected to rapid thermal oxidation (RTO) at temperatures ranging from 350°C to 500°C and annealing time between 1/4 to 16 minutes. The TiN top electrodes were deposited by PVD afterwards.

Oxidation Temperature Dependence

The electrical properties for WO_X devices under different RTO temperature with 1 minute oxidation time were studied. Figure 1 shows the initial resistance and the WO_X thickness as a function of the oxidation temperature. While the WO_X thickness increases with RTO temperature, the initial resistance increases drastically beyond 450°C from the improvement of WO_X quality. To activate the WO_X device, a forming pulse to bring the cell from low initial resistance state to high resistance state is needed [2]. Figure 2 presents the pulsed R-V curves of the devices with different RTO temperatures under forming, SET, and RESET operations, respectively [3]. As the RTO temperature increases, not only the forming voltage can be reduced but the resistance window can be enlarged (Fig. 3). The maximum cell resistance after 50ns RESET pulse also increases with the RTO temperature (Fig. 4).

While the 500°C-RTO devices having better electrical performance than 400°C-RTO devices, physical analyses including TEM, XRD, and Raman spectra were further utilized to investigate the microstructure for these two groups. The cross-sectional TEM images for devices with 400°C and 500°C RTO show the WO_X thickness are 19nm and 109nm, respectively (Fig. 5(a) and 5(b)). The x-ray diffraction profile from a thin film specimen (Fig. 6) shows significant monoclinic tungsten oxide phase after 500°C RTO. Monoclinic tungsten trioxide has diffraction peaks at 2θ=23.1° and 23.6°, corresponding to planes (002) and (020) (JCPDS 43-1035). Fig. 7 shows the Raman spectra of WO_X from 400°C and 500°C RTO samples. The 500°C sample shows four strongest modes which agree with the well-defined Raman bands on monoclinic WO_3 at 272, 322, 709, and 807 cm^{-1} [4]. According to the XRD and Raman results, the monoclinic WO_3 is formed on the surface of WO_X layer [5] after RTO at 500°C (but not 400°C). This high quality WO_3 layer plays an important role on electrical properties.

Oxidation Time Dependence

The effect of RTO time is further studied. At 500°C RTO, the distribution of the initial resistance remains tight when the RTO treatment is equal or less than 4 minutes. (Fig. 8). It is also found that the oxidation process of the WO_X film follows the silicon oxide growth model proposed by Deal-Grove, et al. [6], which can be expressed as:

$$\mathbf{t = X^2 / B + X / (B/A),} \qquad \mathbf{(1)}$$

where **X** is the WO_X thickness and **t** is the RTO time. **B/A** is the linear rate constant and **B** is the parabolic rate constant. By solving equation (1), **the WO_X thickness** can be expressed as:

$$\mathbf{X = \{-A + (4\,B\,t + A^2)^{1/2}\}/2} \qquad \mathbf{(2)}$$

As shown in Fig. 9, the oxidation thickness at different RTO treatment time can be fitted by this equation very well. Assume the rate constant follows the Arrhenius's law, the oxidized thickness can be plotted as a function of 1/T, where T is the RTO temperature (Fig. 10). From the Arrhenius plot, the calculated activation energy (Ea) of tungsten oxidization is 0.73 eV, close to but smaller than 0.82 eV for the monoclinic WO_3 [7]. With the evidences from the XPS [3] and XRD results, the WO_X layer contains not only WO_3 but also tungsten of other oxidized states, which contribute the reduction of the calculated Ea.

The forming voltage is almost independent of annealing time (Fig. 11), which again indicates the switching of WO_X ReRAM device is at the interface but not the bulk of WO_X film [8]. The increase of SET and RESET voltages with the annealing time in Fig. 11 can be explained by the voltage drop on the thicker WO_X bulk region. The optimized RTO treatment condition is found to be at 500°C for 1 to 4 minutes. With this condition the SET/RESET voltage can be as low as -1V/2V, with the resistance window kept LRS < 10KΩ and HRS > 100KΩ. Fig. 12 shows the hysteresis loops of pulse R-V curve for 500°C/1 minute device. The low operation voltage is obtained without strong degradation indicating good endurance property.

Summary

The resistance switching characteristics of WO_X device is related to the quality of the monoclinic tungsten oxide layer formed at the W-plug surface by the RTO process. The kinetic mechanism for RTO tungsten oxidation can be modeled by Deal-Grove equation and the optimized RTO condition at 500°C/1 minute is sufficient for manufacturing high performance ReRAM devices.

Reference

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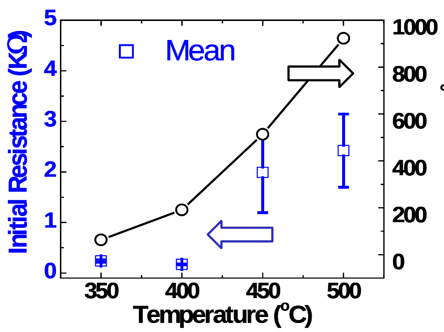

Fig. 1 The initial resistance and WO_X thickness for cells processed by RTO 1 min. at different temperature.

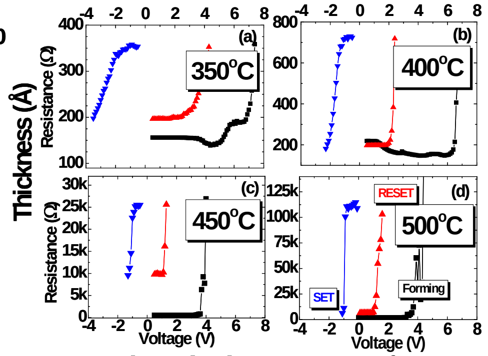

Fig. 2 The pulsed R-V curves of Forming (black), SET (blue) and RESET (red) operations for cells processed by RTO 1 min. at different temperature.

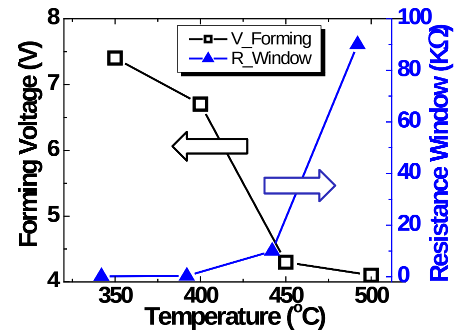

Fig. 3 The forming voltage and resistance window for cells processed by RTO 1 min. at different temperature.

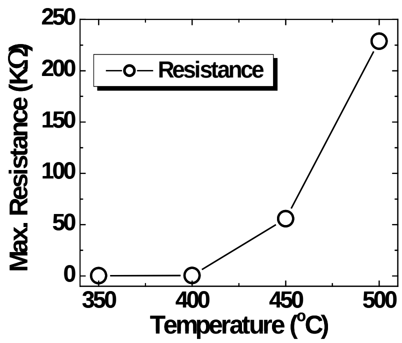

Fig. 4 The maximum resistance for cells processed by RTO 1 min. at different temperatures.

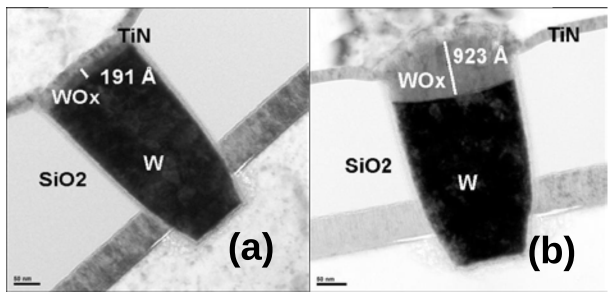

Fig. 5 TEM images of WO_X RRAM element with 0.24μm via diameter by RTO 1 min. at (a) 400ºC, (b) 500ºC.

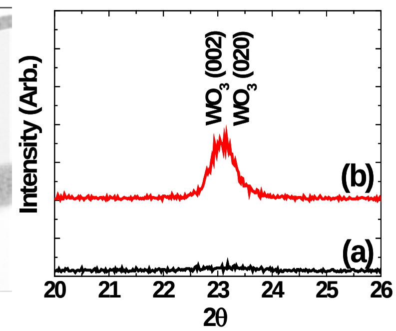

Fig. 6 XRD of WO_X by RTO 1 min. at (a) 400ºC, (b) 500ºC.

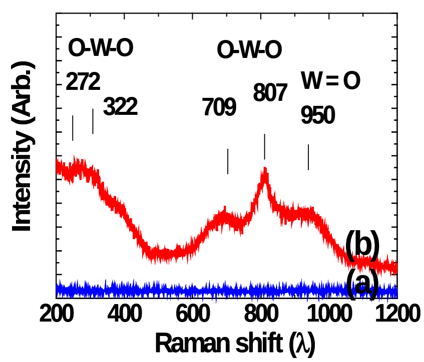

Fig. 7 Raman Spectra of WO_X by RTO 1 min. at (a) 400ºC, (b) 500ºC.

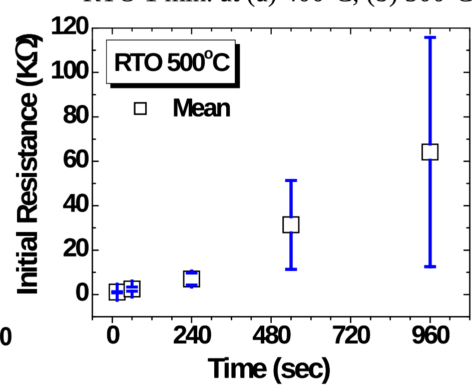

Fig. 8 The initial resistance for cells processed by RTO 500ºC with different time.

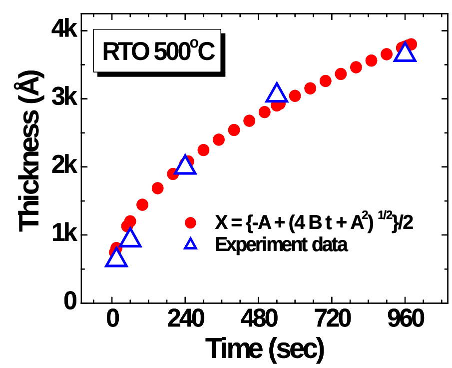

Fig. 9 WO_X thickness versus RTO time, fitted by the Deal-Grove model.

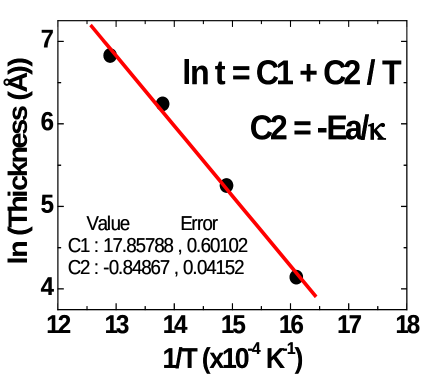

Fig. 10 Arrhenius Plot for the linear rate constant C2, the activation energy is calculated to be Ea = 0.73 eV, the Boltzmann constant κ is 8.61734 eV/K.

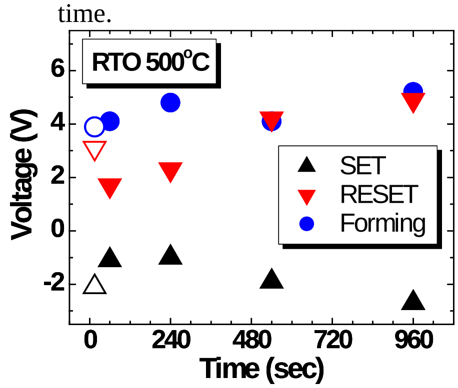

Fig. 11 The forming , SET and RESET voltage at RTO 500ºC for different time. The data points for 15-second process time are abnormal because of the WO_X layer is too leaky.

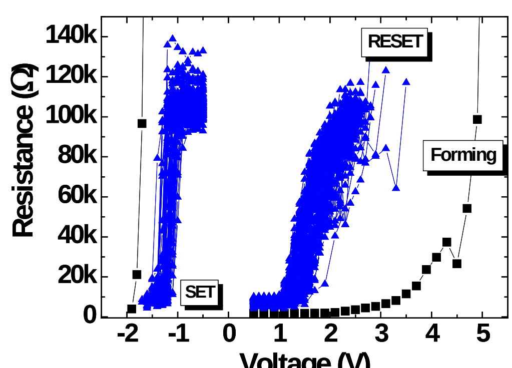

Fig. 12 The 100-cycle performance of the pulsed R-V hysteresis loops for a cell processed at RTO 1 min./500ºC.