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Direct observation of conducting paths in TiO_2 thin film by Transmission electron microscopy

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TiO_2 is one of the most promising materials for ReRAM (resistive random access memory) due to the simple process and low energy operation. A filament model, which ascribes the switching between a low and a high resistance state to the formation and rupture of conducting paths, has been widely accepted as the resistance switching mechanism of binary transition metal oxides, such as NiO and TiO_2. The conducting path is often believed to originate from defects and/or impurities inevitably encountered in most oxides. The microstructures of the filaments, however, have been rarely reported.

Here, we report the direct observation of the filamentary conduction paths in oxide thin film of a Pt/TiO_2/Pt structure. A TiO_2 thin film of 30nm was deposited by plasma enhanced atomic layer deposition process and an array Pt electrodes with a diameter of 100μm on each side of the film is employed for voltage sweeps. The differences between the high resistance state (HRS) and the low resistance state (LRS) of TiO_2 material were investigated using transmission electron microscopy (TEM) and electron energy-loss spectroscopy. Cross section TEM samples were prepared by focused ion beam (FIB) as shown in Fig. 1. Three kinds of samples were prepared. Sample No.1 is taken from the area where the top electrode is exploded. This area is irregularly formed during the set process (HRS→LRS), especially when the top electrode is thin [1]. This explosion is attributed to the excessive formation of oxygen gas, generated as a result of oxygen vacant nature of the filaments. Sample No. 2 and 3 are taken from the area with normal morphology. Sample No. 2 is taken when the stack is in the LRS and No. 3 is taken when it is in the HRS, respectively.

In the 'LRS exploded sample'; sample No. 1, selected area electron diffraction showed peaks from non-stoichiometric Titania (Fig. 2). D-spacing over 3.5Å cannot be observed in normal TiO_2 such as Rutile, Anatase, or Brookite. These non-stoichiometric crystalline phases are determined to be Ti_4O_7 or Ti_5O_9, so called Magneli phase Ti_nO_{2n-1}. Magneli phase is generated by crystallographic shear (CS) plane from the Rutile structure [3]. These phase show metallic behavior at room temperature [2]. The diameter of this conducting phase was about 10~20 nm, and the density of the filaments was higher than the other two samples. In the 'LRS sample'; sample No. 2, we observed a few connected Magneli structures between the top and bottom electrode as shown in Fig. 3a,b. On the other hand, all the observed Magneli structures in the 'HRS sample'; sample No. 3, were disconnected (Fig. 3c,d). These results indicate that connection and disconnection of this metallic Ti_4O_7 and Ti_5O_9 is indeed responsible for the resistive switching. In addition, we observed that this phase has a specific orientation with the Rutile thin film in each case. The orientation of the oxygen deficient CS plane of the Magneli structure may be explained by the anisotropic mobility in this phase.

References

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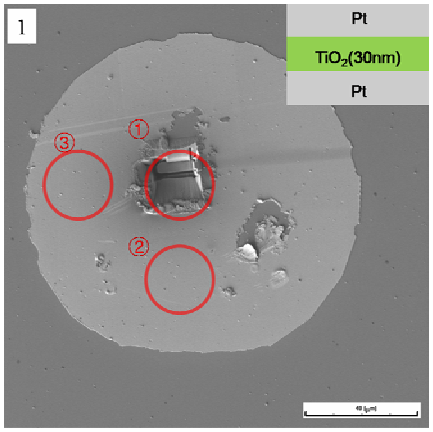

FIG. 1. Top view of the sample by SEM. The stack is described by inserted figure. Each number indicates the area where sample is taken by FIB. Diameter of electrode is about 100μm.

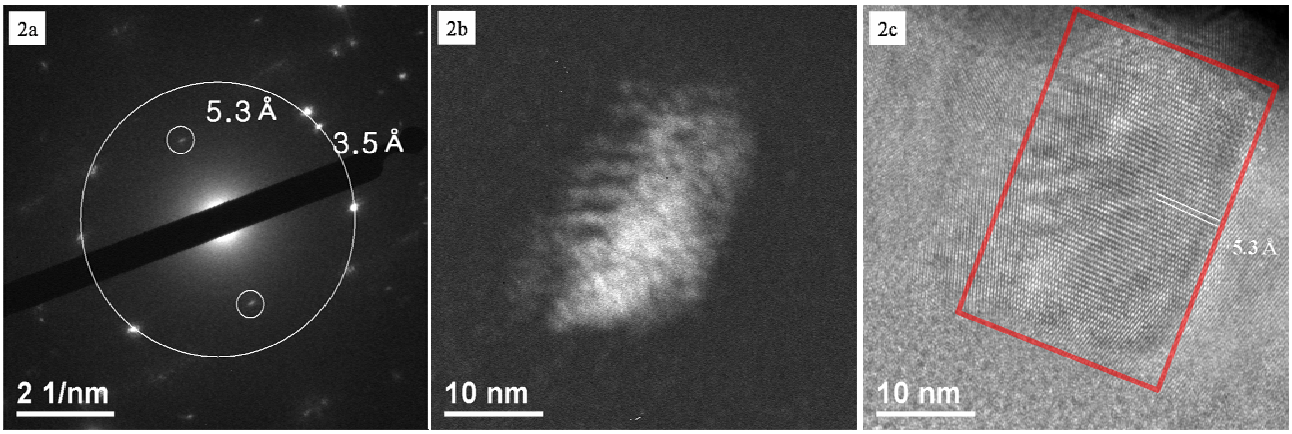

FIG. 2. (a) Selected area electron diffraction of the 'LRS exploded sample' showing non-stochiometric peaks. (b) Dark-field image taken from the peak corresponding to 5.3Å (c) High-Resolution image of the bright area in (b). Bottom of (c) image is the area where electrode is exploded.

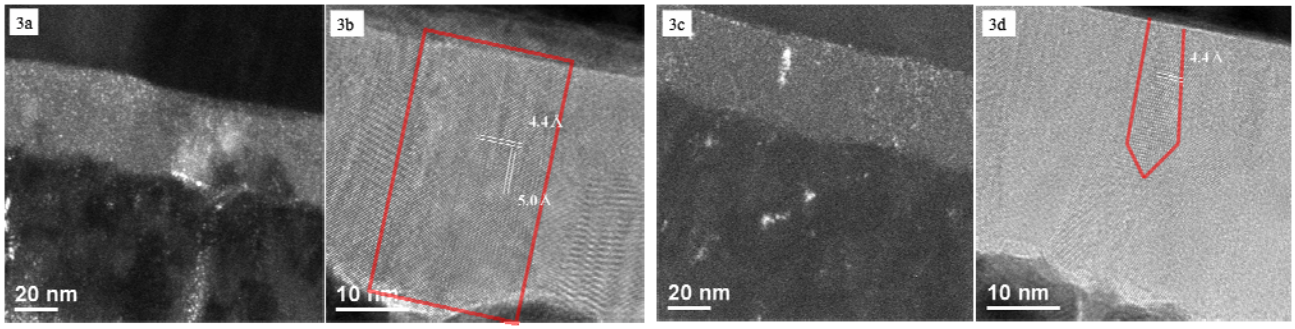

FIG. 3. Dark-field images indicating non-stoichiometric Titania. Connected column of Ti_4O_7 in the 'LRS sample' and disconnected column in the 'HRS sample' are marked. Dark-field image from the 'LRS sample' (a) and its corresponding high resolution image (b). Dark field image from the 'HRS sample' (c) and its corresponding high resolution image (d).

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