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Effect of the top electrode material on the resistive switching of TiO_2 thin film

Wan-Gee Kim, Shi-Woo Rhee *

Laboratory for Advanced Materials Processing (LAMP), Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

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ABSTRACT

Effect of the top electrode (TE) metal on the resistive switching of (TE)/TiO_2/Pt structure was investigated. It was confirmed that the potential barrier height between the metal and TiO_2 is an important factor on the resistive switching characteristics. When high Schottky barrier was formed with the TiO_2 film, using Pt or Au as a top electrode, both stable URS (unipolar) and BRS (bipolar resistive switching) characteristics were observed depending on the current compliance level. In the case of Ag, which forms a relatively low Schottky barrier, only BRS characteristics were observed, regardless of the current compliance level. In the case of Ni and Al, which have similar work function as Ag, unstable URS and BRS at very low current compliance levels were observed due to a chemical reaction at the interface. For the Ti electrode, resistive switching was not observed, because the work function of Ti is lower than that of TiO_2 and TiO phase was formed at the interface (Ti/TiO_x contact is ohmic).

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1. Introduction

Resistive switching induced by an applied electric field has been extensively studied for its potential application in the resistance random access memories (ReRAM). The resistive switching RAM offers a possibility of high density integration, lower power operation, easier down-scaling and CMOS (complementary metal-oxide-semiconductor) compatibility. As one of the reported resistance random access memory materials, TiO_2 [1] has been actively studied for its high on/off resistance ratio, low on/off voltage, and long retention time compared to the other binary transition metal oxides such as NiO [2], Nb_2O_5 [3], and MgO [4].

As for the resistive switching mechanism, there are two factors which are still unclear. One is the effect of defects such as oxygen vacancies in the film [5,6] and the other is the effect of the interface between the metal and the oxide film which is related to the carrier injection [7–10]. It is believed that the contact between the metal and the oxide plays a crucial role in the resistive switching process and research efforts have been focused on the effect of the electrode material on the resistance switching properties. In the case of the p-type binary oxide such as NiO [7] and Cu_2O [8], it was reported that an ohmic contact or a low Schottky barrier was needed to apply an effective electric field to the oxide film high enough to induce trapping or detrapping at defect states. In this case, resistive switching was not observed for a well-defined Schottky contact at the interface. As opposed to NiO and Cu_2O, the resistive switching of PCMO [9] (p-type pervoskite oxide: (Pr, Ca)MnO_3) was observed with only Schottky contact. For ZrO_2 [10] (n-type binary oxide) both unipolar and bipolar resistive switching (URS and BRS) were observed depending on the Schottky barrier height at the interface. There are two main mechanisms suggested in the literature for the resistive switching. One is the filamentary mechanism where conducting path is formed and disappears due to the oxygen vacancy (defect control) depending on the applied voltage. This is from the characteristics of the bulk oxide film. The other one is the effect of the interface in the metal-insulator–metal structure (MIM) including the potential barrier height from the metal work function and the Fermi level of the oxide layer. Also at the interface, there can be a chemical reaction driven by the chemical potential (M1 + M2O → M1O + M2) for some metal, M1 and M2. It seems that one model cannot explain all the experimental observations and more than one effect may be involved in the resistive switching process.

So far, the electrode material dependence on the resistive switching properties of TiO_2 films has not been reported. In this paper, the dependence of the switching properties of TiO_2 films on the top electrode material was evaluated for (TE: top electrode)/TiO_2/Pt MIM structure with various top electrode material such as Pt, Au, Ag, Ni, Al, and Ti. The effect of interfacial reactions and interlayer formation was also studied.

2. Experiment

TiO_2 thin films were deposited with an rf magnetron sputtering system on Pt/Ti/SiO_2/Si substrate. Pt on Ti/SiO_2/Si substrate with 150 nm thickness was used as a bottom electrode (BE). A Ti metal target (50.8 mm, 99.995%, SHENZHEN, China) and a gas mixture of

* Corresponding author. Tel.: +82 54 279 2265; fax: +82 54 279 8619.
E-mail address: srhee@postech.ac.kr (S.-W. Rhee).

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Table 1
The work function (eV) of TiO_2 and electrode metals measured with ultraviolet photoemission spectroscopy (UPS).

TiO_2	Pt	Au	Ag	Ni	Al	Ti
4.05	5.1	4.85	4.3	4.5	4.25	3.9

Ar and O_2, at a mixing ratio of 10:1, were used to deposit the TiO_2 thin films. During the deposition of the TiO_2 thin films, the rf power and substrate temperature were maintained at 150 W and room temperature, respectively. The base pressure of the deposition chamber was maintained below 8×10^{-6} torr by a rotary vane pump and a turbo molecular pump and the working pressure was 7×10^{-3} torr. The thickness of the TiO_2 film was 50 nm for all the experiment.

After the deposition of TiO_2, to make a metal-insulator–metal (MIM) structure, various metals such as Pt, Au, Ag, Ni, Al, and Ti were deposited as a top electrode (TE) on the oxide surface through a shadow mask to form circular dots with 100 µm diameter. TE's were deposited using a DC magnetron sputtering system (Pt, Ag, Ni, and Ti) or a thermal evaporator (Au and Al).

Ultraviolet photoemission spectroscopy (UPS) was used to measure the work function of the film, scanning electron microscopy (SEM) was used to measure the film thickness, atomic force micrograph (AFM) was used to measure the surface morphology, X-ray diffraction (XRD) was used to check the crystallinity and X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used to measure the film composition. The current–voltage (*I–V*) characteristics of the MIM structure were measured at room temperature and ambient pressure, using a precision semiconductor parameter analyzer (Agilent 5270A). In this exper-

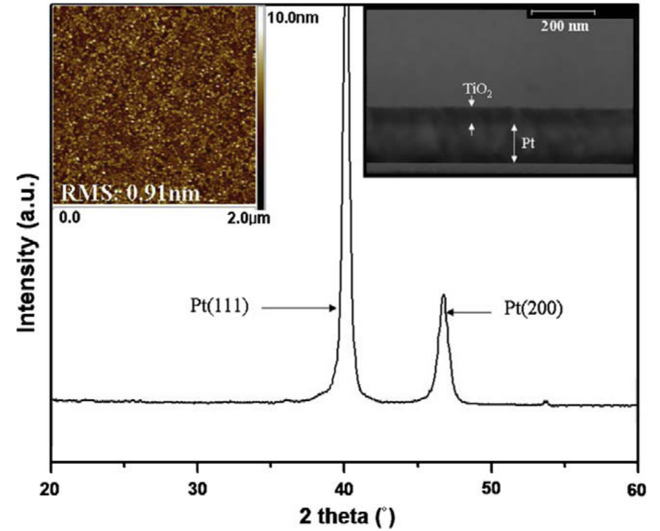
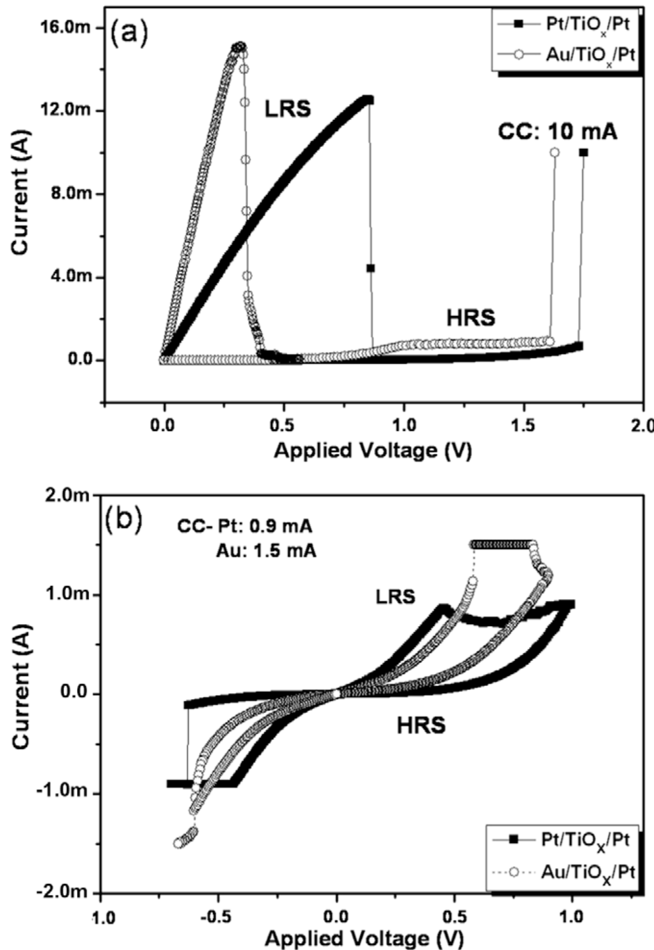


Fig. 1. AFM, SEM micrographs and X-ray diffraction peak for the TiO_2 film deposited on Pt film.



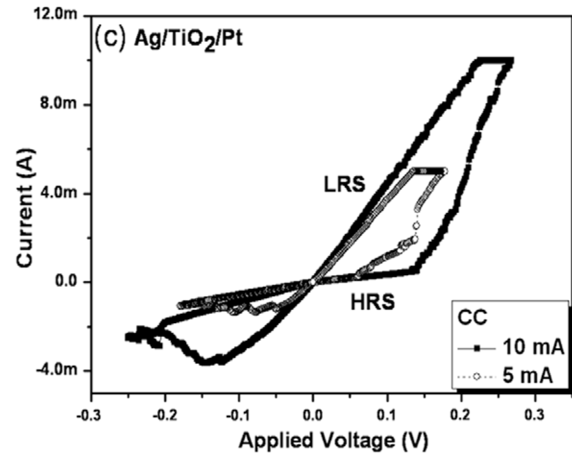


Fig. 2. *I–V* characteristics of the TE/TiO_2/Pt structure with top electrode material of Pt and Au at the current compliance (CC) of (a) 10 mA, at (b) 0.9–1.5 mA and (c) Ag at the CC of 10 mA and 5 mA.

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