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Improvement of Reliability by Using Fluorine Doped Tin Oxide Electrode for Ta_2O_5 Based Transparent Resistive Switching Memory Devices*

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Purpose: Fluorine doped tin oxide (FTO) bottom electrode for Ta_2O_5 based RRAM was studied to apply for transparent resistive switching memory devices owing to its superior transparency, good conductivity and chemical stability.
Methods: ITO/Ta_2O_5/FTO (ITF) and ITO/Ta_2O_5/Pt (ITP) devices were fabricated on glass and Si substrate, respectively. UV-visible (UV-VIS) spectroscopy was used to examine transparency of the ITF device and its band gap energy was determined by conventional Tauc plot. Electrical properties, such as electroforming and voltage-induced RS characteristics were measured and compared.
Results: The device with an FTO bottom electrode showed good transparency (>80%), low forming voltage (~-2.5V), and reliable bipolar RS behavior. Whereas, the one with Pt electrode showed both bipolar and unipolar RS behaviors unstably with large forming voltage (~-6.5V).
Conclusion: Transparent and conducting FTO can successfully realize a transparent RRAM device. It is concluded that FTO electrode may form a stable interface with Ta_2O_5 switching layer and plays as oxygen ion reservoir to supply oxygen vacancies, which eventually facilitates a stable operation of RRAM device.

Keywords: Resistive Switching Memory, Transparent Conducting Oxide, Bipolar Resistive Switching, Unipolar Resistive Switching, Conducting Filament

1. Introduction

Computing memories has been successively improved their performances, such as high density, high speed and low power consumption[1-3]. Conventional charge-based memories, such as DRAM and flash memories, become more harsh to maintain its charge density per working cell while scaling limits the physical dimension of the device [3]. On the other hand, resistive random access memory (RRAM) has become remarkable due to its simple structure, fast switching speed, excellent scalability, low energy consumption, and compatibility with existing semiconductor technology[1-5].

In general, an RRAM cell has a conductor/insulator /conductor structure, in which based on the resistive switching (RS) phenomena of an insulating layer[6, 7]. Transition

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metal oxide materials have been extensively studied for understanding of its RS mechanism. One of the prevailing theory for RS mechanism is that the migration of oxygen vacancies and ions under applied voltage is responsible for the formation and annihilation of conducting filaments between the two electrodes[1, 3]. Controlling RS of set (change from high-resistance-state to low-resistance-state) and reset (opposite direction to set) performances conforms to form or impair the conducting filament (CF). Generally, there are two types of RS - bipolar and unipolar - the former requires inversed polarity of voltage bias to set and reset, while the latter does not matter the polarity. Note that both types of RS may coexist in the same device as well[4, 8-11].

Among abundant oxide-based materials, in this study, fluorine doped tin oxide (FTO) was focused on for transparent RRAM application[12, 13]. FTO has been known for its transparency, electrical conductivity, and chemical resistance. Basically tin oxide is a wide band-gap semiconductor that has high optical transparency. Furthermore, by doping fluorine, electrical resistivity can be significantly reduced because fluorine dopants and oxygen vacancies produce the high carrier concentration[14, 15]. Optical and electrical properties of Ta_2O_5-based RRAM devices with FTO and Pt electrode were compared in this study.

2. Experimental Procedure

Two types of devices, ITO/Ta_2O_5/FTO (ITF) on soda-lime glass substrate and ITO/Ta_2O_5/Pt/SiO_2 (ITP) on silicon substrate and were fabricated, respectively, as shown in <Fig. 1 (a)> and <Fig. 1 (b)>. Bottom electrode, FTO and Pt, was deposited by sprayed pyrolysis deposition and e-beam evaporation, respectively. 10nm-thick Ta_2O_5 switching layer was deposited on both substrates by plasma enhanced atomic layer deposition at 250°C. Then, 50nm-thick ITO as top electrode was formed on both devices by radio frequency(RF) sputtering using shadow mask.

Transmittance of ITF device was characterized by UV-VIS (Lambda 35) on a range of 300~1100 nm of wavelength. Band gap energy was estimated by Tauc plot from absorption coefficient.

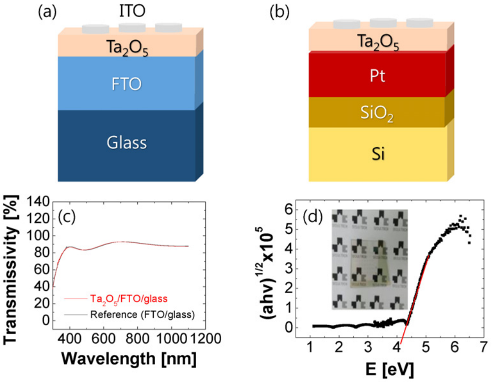

Fig. 1 Schematic diagrams of (a) ITO/Ta_2O_5/FTO device on glass and (b) ITO/Ta_2O_5/Pt device on Si. (c) transmittance of the Ta_2O_5/FTO/glass and reference sample (FTO/glass). (d) tauc plot of the Ta_2O_5/ FTO/glass from transmittance and determination of band gap energy (inset: picture of transparent ITF device on glass)

To analyze the electrical property, semiconductor parameter analysis equipment (HP-4156, Agilent) was employed for measuring quasi-static (DC) I-V characteristics. All the electrical measurements were conducted at room temperature.

3. Results and Discussion

Optical property of ITF device compared to reference sample (FTO film on glass) was characterized under the UV-Visible wavelength range. ITF device showed 85 - 90 % transmittance on visible light (380 nm~800 nm) according to the UV-VIS spectroscopy as shown in <Fig. 1 (c)>. Absorption coefficient extracted from transmittance and plotted as Tauc plot shown in <Fig. 1 (d)>. Indirect band gap energy was determined as 4.32 eV according to the intercept of X-axis, where band gap energy of Ta_2O_5 was reported as 4.5eV. Inserted picture in <Fig. 1 (d)> shows transparent ITF device on glass.

Electrical properties of ITF and ITP devices were characterized. In order to measure the forming voltage, positive and negative bias voltage were applied on ITO top electrodes, while Pt or FTO electrodes were grounded. Prior to the forming process, I-V characteristics of the pristine devices were observed from -1V to 1V (data not shown). Both devices showed asymmetric I-V curves resulting from the different top and bottom electrode materials. Generally, FTO has

smaller work function (4.4 eV) compared to that of ITO (4.7 eV) or Pt (5.1~5.9 eV), larger leakage current is expected. In other words, electron can be easily injected from the FTO side. Whereas, it is hard to inject electrons from Pt side, thus lower current level was observed compared to that of FTO.

Such a difference in the electron injection may lead disparate forming behaviors. Forming under positive and negative bias voltage was examined from ITF and ITP devices as shown in <Fig. 2>. Forming voltage of ITF device under negative (positive) bias was ~-2.5 V (~+4.5 V) as shown in <Fig. 2>. Therefore, lower forming voltage was required under negative bias voltage. On the other hand, forming voltage of ITP device showed opposite polarity dependency (+3.5 V and ~-6.5 V). That is, lower forming voltage was required under positive bias voltage. It was noted that forming voltage of ITF (~-2.5 V) device under negative bias was much lower than that of ITP (~-6.5 V) device. It can be understood that fluent electron injection from FTO electrode could significantly reduce the forming voltage. Forming voltage under positive bias on ITO was in the middle of forming voltage under positive bias on FTO and Pt electrode.

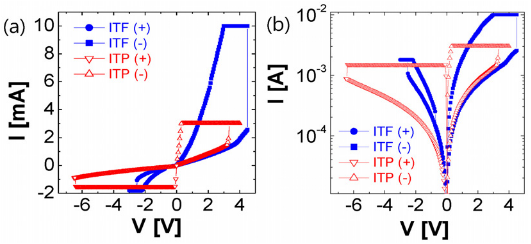

Fig. 2 Forming under positive and negative bias voltage was examined from (a) ITF and (b) ITP devices, where forming voltage of ITF device under negative (positive) bias was −2.5V (+4.5 V) and ITP device showed opposite polarity dependency (+3.5 V and −6.5 V)

In the following, RS characteristics were examined on both devices. In case of ITF, forming process was performed under negative bias voltage. After that the reset process occurred at ~+3.5 V, which means the device transited to high-resistance-state (HRS) as shown in <Fig. 3 (a)> and <Fig. 3 (b)>. And then the set process occurs at ~-2.3 V meaning the resistance of the device transit to low-resistance-state (LRS). In other words, bipolar RS behavior was observed in the ITF device. Note that both LRS and HRS exhibited nonlinear I-V hysteresis. Even forming process was conducted under positive bias voltage, bipolar RS under negative set and positive reset were dominantly observed. This means that ITO/Ta_2O_5 top interface is responsible for the switching. Detailed explanation will be followed later in this section.

Next, RS characteristics of ITP device were shown in <Fig. 3 (c)> and <Fig. 3 (d)>. In this case, forming process was performed under positive bias voltage, because forming under negative voltage gave birth to the irreversible breakdown owing to the high forming voltage (data not shown). After positive forming, bipolar RS was observed as well. Reset process occurred at ~-0.8 V and then set process was followed at ~+0.5 V. However, linear I-V hyste-

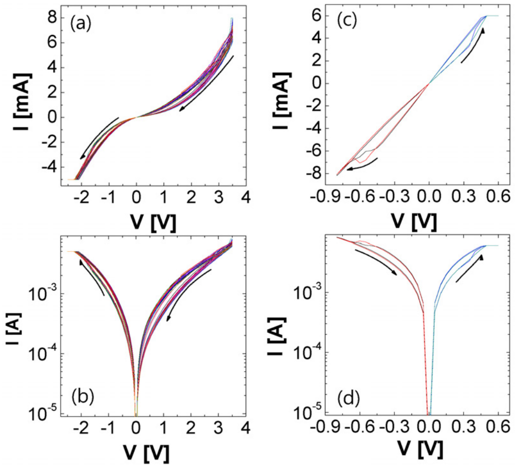

Fig. 3 I−V curves of BRS in ITF device in (a) linear and (b) semi−log scale and those of ITP devices in (c) linear and (d) semi−log scale

resis both under HRS and LRS were shown and such a high linearity and low switching voltage are known as the general RS behaviors of Ta_2O_5 based RRAM device. Contrary to ITF device, bipolar RS under positive set and negative reset means that Ta_2O_5/Pt bottom interface is responsible for the switching.

Occasionally the ITP device showed unipolar RS behavior. In this case, forming process occurred at positive polarity, then the reset and set process occurred under negative bias voltage as shown in <Fig. 4 (a)>, <Fig. 4 (b)>. Firstly reset process occurred at -1V, and then set process occurred again from -1.5 to -1.8V. Note that huge reset which means large increase in the resistance was observed compared to bipolar RS. When it comes to the reliability of the RRAM device, bipolar RS is more reliable showing higher cyclability even though it has smaller resistance ratio than that of URS. In addition, ITP device showed both bipolar and unipolar RS randomly so that it is hard to expect and control the RS behavior.

The RS mechanisms of ITF and ITP devices were considered in the following. Based on the forming and polarity of bias voltage for bipolar RS of ITF, it is considered that oxygen vacancies are more easily generated from FTO electrode under negative voltage. Even in the pristine state, oxygen vacancies can exist between Ta_2O_5/FTO interface owing to the high oxygen affinity of Ta_2O_5 layer. These positively charged vacancies are piled up toward ITO top electrode under negative bias and eventually form the conducting filament and resistance state changes from HRS to LRS(that is, forming and set process). Under positively applied voltage, oxygen vacancies are moved back to FTO electrode and the conducting filament is disconnected and resistance state changes to HRS (reset process). <Fig. 5 (a)>~<Fig. 5 (c)> show the schematics of bipolar RS of the ITF device. The interface between ITO and Ta_2O_5 is considered to the switching interface and FTO works as reservoir of oxygen vacancy as well as electrode. Note that high concentration of oxygen vacancies at the interface prevents from the formation of Ohmic contact, which results in then on linear I-V hysteresis in ITF device.

On the other hand, ITP device exhibited both bipolar and unipolar RS behaviors after positive forming process. It is considered that oxygen vacancies are generated and piled up from ITO electrode. Conducting filament is formed when the piled oxygen vacancies are connected between the electrodes. Applying negative voltage makes oxygen vacancies move back to ITO electrode and reset process occurs. In this case, interface between Ta_2O_5 and Pt is considered as switching interface as shown in <Fig. 5 (d)>~<Fig. 5 (f)>.

Unipolar RS of ITP had a little difference with that of bipolar RS. After positive forming process, middle of

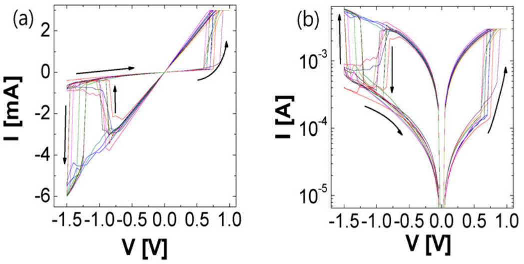

Fig. 4 In case of URS in ITP, forming process occurred at positive direction, then the reset and set process occurred under negative bias voltage. Reset process occurred at −1 V, and then set process occurred at a range from −1.5 to −1.8 V

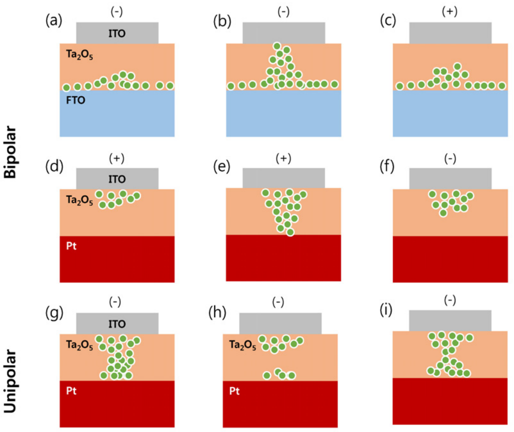

Fig. 5 (a−c) Schematics of BRS filament structure in ITF of their forming, reset, and set pro−cesses. (d−f) BRS in ITP, (g−i) URS in ITP conducting filament is broken and thus oxygen vacancies are remained not only at ITO side but also at Pt electrode as shown in <Fig. 5 (h)>. This can happen when the preformed conducting filament is strong and thereby thermochemical oxidation of conducting filament occurs by excessive joule heating. When large negative voltage is applied, oxygen vacancies reached in the middle of the broken filament in Ta_2O_5 layer, and LRS can be recovered. <Fig. 5 (g)>~<Fig. 5 (i)> represent the schematics of unipolar RS in ITP device.

The reason of reliable RS observed from ITF is considered as follows; (1) it is known that FTO contains high concentration of oxygen vacancies owing to the nature of intrinsic SnO_2 material. Therefore, FTO can serve as reservoir of oxygen ion species. Even ALD-grown Ta_2O_5 is hyper-stoichiometric owing to the growth condition, the reseems to be less oxygen vacancies content expected. Therefore, the role of FTO reservoir is even more important. (2) FTO has lower work function compared to Pt, electron can be easily injected and thus forming occurs at lower voltage. Injected electrons may accelerate the ionization of oxygen in Ta_2O_5 near the interface between the FTO and Ta_2O_5. (3) Chemically inert nature of FTO can enhance the reliability of RS behavior. However, the interface between ITO and Ta_2O_5 is considered as switching interface in ITF device, it is important to examine the endurance of ITF device, which is remained as the future work.

4. Conclusion

In this study, optical and electrical characteristics of the Ta_2O_5 based RRAM device with FTO bottom electrode and ITO top electrode were investigated. RRAM device showed 85~90% transmittance on visible light. The device also showed lower forming voltage and reliable bipolar RS behavior with non-linear I-V characteristics. It was believed that ALD-grown Ta_2O_5 could form a stable interface with FTO bottom electrode. Through this work, FTO as one of the transparent conducting oxide (TCO), can indeed realize a transparent RRAM device. FTO electrode may work as oxygen reservoir to supply oxygen vacancies and ions, and thus reliable RS characteristics could be achieved.

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