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Novel Non-Precious Metal Electrode Material for ReRAM Device

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Abstract

This paper describes the development of novel non-precious metal electrode material which has excellent cost effectiveness for ReRAM devices. The replacement of the bottom electrode (BE) from Pt to TiN does not influence the excellent switching property of ReRAM-cell, while the replacement of the top electrode (TE) deteriorates the switching property. This is due to low O_2 barrier properties of TiN film and an influence on Ta_2O_5 by N_2 plasma in sputtering process. To solve the issue in TE, conductive diamond like carbon (DLC) films are examined. As a result, excellent switching properties equivalent to TE-Pt are obtained in ReRAM-cell using dense TE-DLC with high sp3 ratio.

1. Introduction

Resistive Random Access Memory (ReRAM) is one of the candidates for next generation non-volatile memory, because it shows excellent performance in speed and power consumption in comparison with other non-volatile memories. In recent years, as a part of the development of high-performance binary oxide ReRAM, studies of a bi-layer structure ReRAM have been reported [1-3]. To replace the NAND flash memory as the mainstream of storage, manufacturing cost needs to be reduced. Electrodes for ReRAM devices need expensive precious metal materials such as Pt in inactive to oxygen, because oxygen movement between the bi-layers is the key to ReRAM operation.

To find alternatives to Pt electrodes, we carry out the development of non-precious metal electrode materials such as TiN and DLC for ReRAM device. Deposition of electrode materials is done by sputtering at low manufacturing cost.

2. Experimental

Ta_2O_5/TaO_x film was deposited on a 12inch-Pt/SiO_2/Si or TiN/SiO_2/Si substrate as a BE by a multi chamber type production tool (ENTRON-EX W300, ULVAC). 50μm diameter TE-Pt, TiN, or DLC was deposited by magnetron sputtering using a shadow mask. Switching properties of TE/Ta_2O_5/TaO_x/BE-ReRAM-cell was measured by a semiconductor device analyzer (B1500A, Agilent).

3. Results and discussion

Switching property of ReRAM with TiN electrodes

Fig. 1 shows the switching property of Pt/Ta_2O_5/TaO_x/Pt-ReRAM. Operation current is less than 100μA. Reset and set voltage are +1.5V and -1.0V. On/Off ratio at +0.5V is more than 50 [3]. TiN film is prepared by N_2 reactive sputtering using Ti target. Fig. 2 shows the switching property of ReRAM-cell using TiN/SiO_2/Si substrate as BE. This ReRAM cell has performance equivalent to ReRAM-cell with BE-Pt (Fig. 1). However, in the case of using TE-TiN (Fig. 3), switching operation of ReRAM-cell needs forming, high voltage, and high current. To examine the influence of N_2 plasma during sputtering process, Fig. 4 shows the switching property of ReRAM-cell using TE-Pt prepared by Ar and N_2 mixed sputtering gas. This ReRAM needs the forming compared with Fig. 2. This is due to a formation of TaON layer with high electric insulation between TiN and Ta_2O_5 layer (Fig. 5a). This intermediate layer is confirmed in the STEM image (Fig. 5c). Operation current during switching is high overall owing to forming. In Fig. 3, on current and off current at +0.5V are 1.8mA and 0.12mA. In Fig. 4, on current and off current at +0.5V are 2.0mA and 0.50mA. On current is equal to each other, but off current of TE-TiN is higher than it of TE-Pt. This is due to a decrease in the insulation of Ta_2O_5 layer caused by oxygen diffusion to TE-TiN (Fig. 5b).

Development of conductive DLC for top electrode

We focus on cost effective DLC films which has high O_2 barrier properties without N_2 gas during sputtering process [4]. Three types of DLC films are prepared under different conditions A, B, and C [5]. Fig. 6 shows a XRD pattern of DLC films in each condition. Each DLC film has amorphous structure. Fig. 7 shows a Raman spectrum of these DLC films. These DLC films have D band ($1330cm^{-1}$) due to sp2 fraction and G band ($1580cm^{-1}$) due to sp3 fraction [6]. These band peaks are separated by Gaussian fitting. The peak area derived from D band and G band are I_D and I_G. The I_G/I_D ratio of Condition A, B, and C are 2.8, 3.4, and 4.1 respectively. Condition C obtains DLC films with a dense structure and high concentration of sp3 fraction. Therefore, this DLC film is the highest in density ($2.5g/cm^3$) in the XRR measurement of each condition (Table I).

The switching properties of ReRAM-cell using TE-DLC of Condition A (Fig. 8a) and B (Fig. 8b) are deteriorated because DLC film with low density is low oxygen barrier properties. In contrast, ReRAM-cell using dense DLC films of Condition C (Fig. 8c) as TE obtains the same excellent switching properties compared with TE-Pt (Fig. 1). Endurance properties of TE/Ta_2O_5/TaO_x/TiN-ReRAM-cells using the TE-Pt (Fig. 9a) and TE-DLC of Condition C (Fig. 9b) are shown. Both ReRAM-cells operate in less than 100μA and 10^{10} cycles without deterioration.

4. Conclusions

We develop the cost effective non-precious metal electrode and preferable film properties for ReRAM devices. Good switching property is not obtained with TE-TiN and low density TE-DLC because of low oxygen barrier properties. ReRAM-cell using dense DLC films with high sp3 ratio as TE is achieved the same excellent and stable switching properties compared with the ones of Pt precious metal electrode.

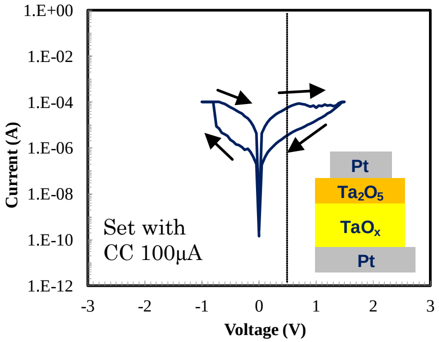

Fig. 1 Switching property of $Pt/Ta_2O_5/TaO_x/Pt$-ReRAM.

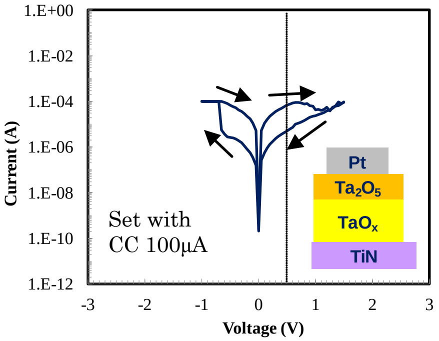

Fig. 2 Switching property of $Pt/Ta_2O_5/TaO_x/TiN$-ReRAM.

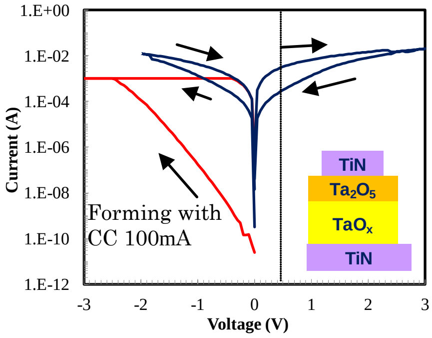

Fig. 3 Switching property of $TiN/Ta_2O_5/TaO_x/TiN$-ReRAM.

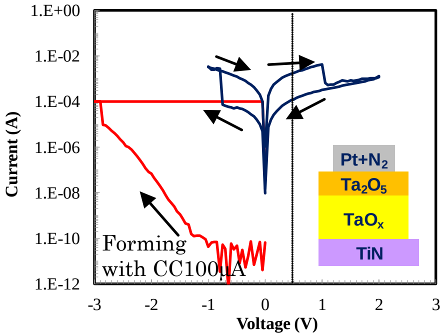

Fig. 4 Switching property of $Pt+N_2/Ta_2O_5/TaO_x/TiN$-ReRAM.

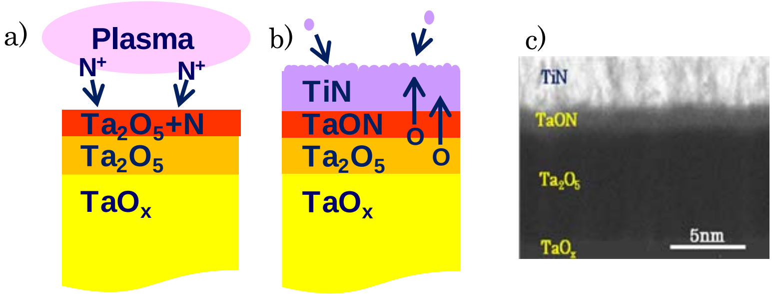

Fig. 5 Schematic figure for the deterioration of switching property by (a) nitridization of Ta_2O_5 surface and (b) oxygen diffusion from Ta_2O_5 to TiN layer. (c) STEM image shows the TaON layer between TiN and Ta_2O_5 layer.

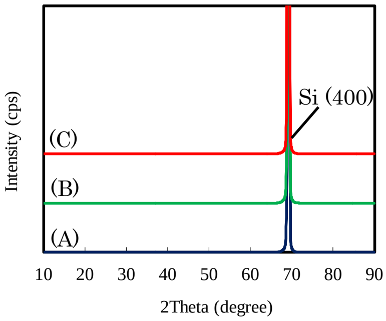

Fig. 6 XRD pattern of DLC films in each condition.

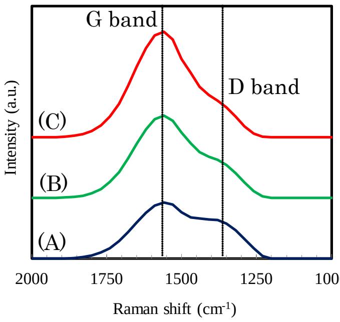

Fig. 7 Raman spectrum of DLC films in each condition.

Table I Various properties of DLC films in each condition

Item	measurement	Codition		
		A	B	C
Crystalline	XRD	Amorphous	Amorphous	Amorphous
I_G/I_D ratio	Raman spectroscopy	2.8	3.4	4.1
Density (g/cm^3)	XRR	1.9	2.0	2.5

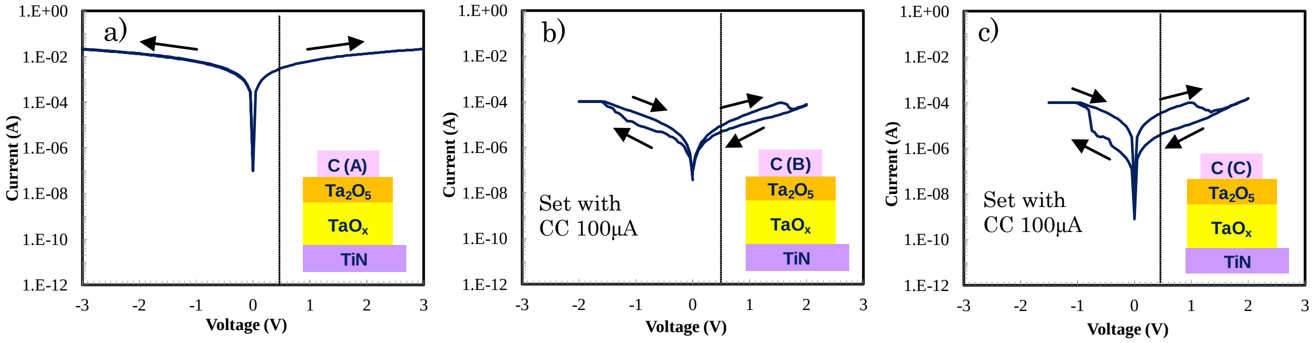

Fig. 8 Switching properties of $TE/Ta_2O_5/TaO_x/TiN$-ReRAM using TE-DLC prepared in (a) Condition A, (b) Condition B, and (c) Condition C.

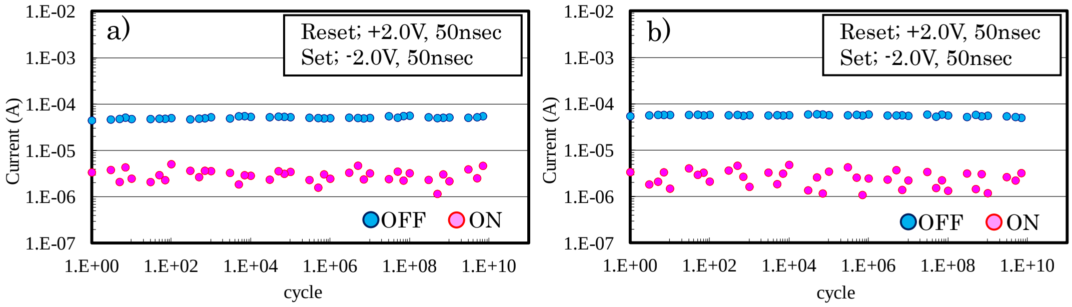

Fig. 9 Endurance properties of $TE/Ta_2O_5/TaO_x/TiN$-ReRAM-cells using (a) TE-Pt and (b) TE-DLC of Condition C. Read voltage is +0.5V both.

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