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Fabrication of Rectifying Pt/TiO_x/Pt by RF-Magnetron Sputtering

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1. Introduction

Titanium oxide (TiO_x) has attracted significant attention as a material of wide application, such as photocatalysts and nanoscale electronic devices. Strukov *et al.* has reported TiO_x as a memristor material which was reasoned by Leon Chua in 1971.[1, 2] A memristive switching was found in micrometer- and nanoscale Pt/TiO_x/Pt structures, with an ON/OFF conductance ratio of ~1000.[3] The current-voltage (*I-V*) curve of the ON state is symmetric, while that of the OFF state is asymmetric, which is similar to that of the virgin state. Most recently, a novel rectifying switch characteristic has been firstly demonstrated in a simple Pt/TiO_x/Pt structure with an ON/OFF ratio of ~100 in our group.[4, 5] Besides memristive and rectifying switching, a field programmable rectifying behavior has been also reported in rutile TiO_2 crystal.[6] In most devices, rectifying *I-V* curve is always observed, which is considered important to realize those switch behaviors. In the previous study, we demonstrate that rectifying characteristic of Pt/TiO_x/Metal is controlled by the electronegativity rather than the work function of the metals. A rectifying *I-V* behavior can be obtained by using metals which are difficult to react with TiO_x.[7] In Metal/TiO_x/Metal structure, careful controlling of TiO_x deposition condition is also important to obtain rectifying *I-V* curves of the devices in their initial state.

In this work, we have investigated the influence of deposition parameter such as O_2 flow in the working gas mixture and the working gas pressure on the *I-V* curve of the device. To improve the rectifying characteristic of the prepared device, effect of post annealing has been also studied.

2. Experiments

According to the previous study, Pt was selected as bottom (BE) and top electrodes (TE). The TiO_x layer was fabricated by radio frequency (RF) sputtering. RF power was 200 W, and working pressures are 0.3, 0.5, 1.0 and 2.0 Pa for Ar gas flow of 4.5, 7.5, 15, and 30 sccm, respectively. O_2 gas flow varies from 0.2 to 1.0 sccm. Thickness of the TiO_x layer in all the devices are 40~50 nm. The conventional photolithography process was used to fabricate rectangular shaped TEs , with size of 30×30 um^2. The dc *I-V* is acquired with a Keithley 4200 semiconductor parameter analyzer. Resistance was measured by four-probe method. Post annealing process was carried out in a muffle furnace in air.

3. Results and discussion

Figure 1 shows the dependence of deposition ratio on the O_2 flow when the Ar flow and working pressure is 15 sccm and 1.0 Pa. An abrupt decrease of deposition ratio has been found at an O_2 flow about 1.0 sccm due to transition from a metal mode to an oxide mode [8]. Deposition ratio as a function of O_2 flow has been also confirmed at the working pressure of 0.5 Pa and 2.0 Pa, respectively.

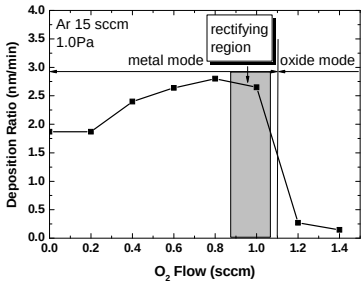

Fig. 1 Deposition ratio as a function of O_2 flow when Ar flow and working pressure are 15 sccm and 1.0 Pa.

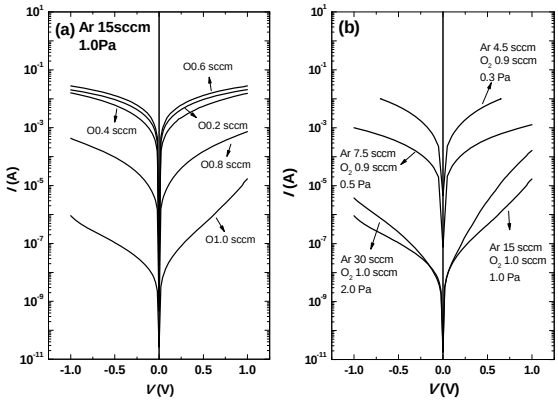

Fig. 2 *I-V* curves of Pt/TiO_x/Pt: (a) TiO_x was prepared at 1.0 Pa with Ar flow of 15 sccm; (b) TiO_x was prepared close to oxide mode (rectifying region in Fig. 1).

As shown in Fig. 2(a), in the devices with the TiO_x layer fabricated at 1.0 Pa, rectifying *I-V* characteristic is only found in the device with the TiO_x layer when the O_2 gas flow is as high as 1.0 sccm. Other devices with TiO_x layer prepared at low O_2 flow exhibit only symmetric *I-V* characteristics.

In all the prepared devices, rectifying behavior was only found in the devices with the TiO_x layer fabricated close to the oxide mode, as shown in Fig. 2(b). Therefore, we call the region close to the oxide mode as rectifying region, as signed in Fig. 1. However, devices with the TiO_x prepared at low working pressure of 0.3 and 0.5 Pa exhibit only symmetric *I-V* behavior. Change from symmetric to

rectifying *I-V* behavior has not been found as well as that found at high working pressure of 1.0 and 2.0 Pa, as shown in Fig. 2 (a).

Rectifying *I-V* behavior of the Pt/TiO_x/Pt is attributed to the Ohmic contact of BE/TiO_x interface and Schottky barrier of TiO_x/TE interface. As an n-type semiconductor, Schottky barrier is expected to be formed at TiO_x/Pt interface. However, this Schottky barrier could be collapsed by the corresponding interface states.[3]

It is assumed that an intrinsic-dead layer is produced at the beginning of the deposition processing, which contributs to the Ohmic contact of BE/TiO_x, due to the extensive concentration of defects in this intrinsic-dead layer. This layer is always reported in dielectric/metal interfaces, such as (Ba, Sr)TiO_3/Pt and $SrTiO_3$/Au,[9, 10] and existence of it could be confirmed by studying the dependence of capacitance on thickness of the TiO_x layer, and this part of work is in progress.

For TiO_x/TE interface, the interface state is controlled by the deposition condition. High O_2 partial pressure results in low concentration of the defects in TiO_x layer, therefore, a Schottky barrier would be obtained. The dependence of resistance on the O_2 flow has been also studied. With an increase of O_2 flow, resistance of TiO_x increases, as shown in Fig. 3. It agrees well to our assumption that defect concentration decreases with O_2 flow during deposition.

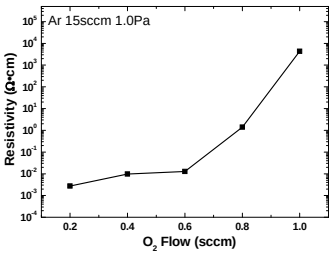

Fig. 3 Dependence of resistivity of TiO_x on the O_2 flow when Ar flow and working pressure are 15 sccm and 1.0 Pa.

To further improve the rectifying property of the devices, effect of post annealing treatment is studied. Post annealing was carried out on the Pt/TiO_x/Pt devices. Figure 4 shows that rectifying ratio at ±1.0 V increase from 20 to 4×10^3 if annealing at a low temperature of 200~300 °C.

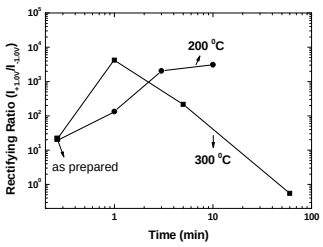

Fig. 4 Dependence of rectifying ratio at ±1.0V on post annealing temperature and time. (TiO_x deposition condition: RF200 W, Ar 30 sccm, O 1.0 sccm, 2.0 Pa)

I-V curves of annealed Pt/TiO_x/Pt are also studied, which did not show here. It is found that the post-annealing treatment results in a marked drop of the reverse current and a slight decrease of the forward current. It suggests that post annealing process contributes an increase of the effective Schottky barrier height at TiO_x/TE interface. However, long annealing time, such as 30 min at 300 °C, results in insulator-like *I-V* curve, and rectifying ratio becomes negligible as shown in Fig. 4. It is attributed to the increase of the Schottky barrier height at both TiO_x/TE and BE/TiO_x interface.

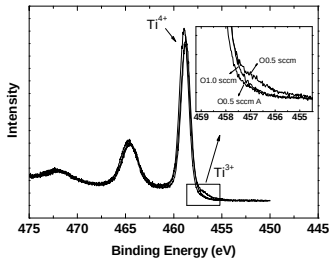

Fig. 5 XPS spectra of the Ti2p region for TiO_x layers: prepared at various O_2 flows: O0.5 (0.5 sccm), O1.0 (1.0 sccm), and O0.5A (fabricated at O_2 flow of 0.5 sccm and annealed in air for 300 °C/30 min). (insert: enlarge of the Ti^{3+} component region) (TiO_x deposition condition: RF200 W, Ar 30 sccm, 2. 0 Pa)

XPS spectra were measured to estimate the alteration of the chemical state of TiO_x layer fabricated in various conditions, as shown in Fig. 5. Ti^{4+} component was found in the all measured TiO_x layers. Only the TiO_x layer prepared at low O_2 flows (O0.5) shows an additional component at 456.6 eV, which corresponds to Ti^{3+} component.[11] It suggests that high O_2 flow during deposition or post annealing treatment results in increasing the Ti ion valence state, which agrees well to the increase of resistivity of TiO_x with O_2 flow and increase of the Schottky barrier height at TiO_x/TE interface due to post annealing.

4. Conclusions

Rectifying Pt/TiO_x/Pt was prepared by RF-magnetron sputtering. An Ohmic contact is always found at BE/TiO_x interface due to the intrinsic-dead layer. *I-V* characteristic of Pt/TiO_x/Pt depends on the TiO_x/TE interface. Devices with TiO_x layer prepared closing to the oxide mode exhibit rectifying properties. By optimize post annealing treatment process, the rectifying ratio at ±1.0V increases from 20 to 4×10^3.

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