Memristive Behaviour of Plasma Treated Titania Thin Films

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***Abstract*—This paper demonstrates the fabrication of based memristive device by sputtering method. Titania thin film was deposited on a glass substrate sandwiched with platinum layer as its metal electrode. The sputtered titania layer was exposed to argon plasma to create the oxygen vacancies that are needed to enhance the memristive behavior. In this work the plasma treatment time was varied for 5, 10, and 15 minutes. In order to analyze the surface TiO_2, we use scanning electron microscopy FESEM. We have also done the Raman measurement analyse phase structure of the titania layer. The reading I-V measurement was taken to analyze the memristive behavior at different plasma treatments. The current-voltage (I-V) was taken at loop 0 V to -5 V, -5 V to 5 V and 5 V to 0 V at every sample. We have observe that the sample with 5 and 15 minutes plasma treat at 1 hour and sample 10 minutes plasma treat at 30 minutes, exhibits better memristive compared before anneal process.**

Keywords-component; memristor; TiO_2; plasma treatment; titania; sputtering.

I. INTRODUCTION

In 1971, theory memristor as fourth circuit element has been discovered by Dr. Leon Chua [1]. The memristor is two terminals device [2]. The memristor's resistance depends on the magnitude and polarity of voltage apply to it and the length of time that voltages has been applied [1-2]. The memristor behave like resistor with dynamic resistance so that the memristance is constant [2]. From Fig. 1 the theory discovered resistor has relationship with current and voltage $(dv = R.di)$ while the capacitor with charge and voltage$(dq = C.dv)$, inductor has relations with magnetic flux and current$(d\varphi = L.di)$. Meanwhile the memristor is device that relates charge to magnetic flux$(d\varphi = M.dq)$.

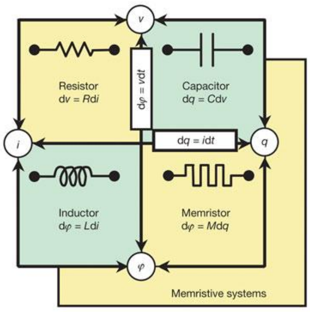


Fig. 1 The four fundamental two-terminal circuit element adapted from [3].

The memristor is basically fabricated with sandwiches of two layer of metal where by titanium oxide layer is deposited between them. The vacancies make the TiO_{2-x} material metallic and conductive [2]. The oxygen deficiencies in the TiO_2 apparent with 'bubbles' of oxygen vacancies scattered throughout the upper layer.

When positive voltage apply on device, the oxygen deficiencies at TiO_{2-x} layer send to the insulating layer TiO_2 as below layer. The cause this boundary of two materials is move down, the percentage of conducting TiO_{2-x} increase. The conductive is more when more positive voltage was applied [2].

Negative charge makes the switch attracts positive charged bubbles and pulling them out of the TiO_2. For this situation, resistive and insulating TiO_2 was increase. The whole switch makes resistive. The cube becomes less conductive when more negative voltage is applied [2]. Either voltage is turned off or on. The oxygen bubbles do not migrate because the boundary both titanium dioxide was frozen. This make the memristor 'remembers' how much voltage was applied.

In addition, the TiO_2 as thin film has low conductive and consider as insulator. When it loses the oxygen its conductivity is become relatively high as a semiconductor [4]. The large number of vacancies is present provide much ratio in dynamic resistance [5].

The TiO_2 are used as thin film because simple constitution and compatibility with standard complementary metal-oxide-semiconductor technology [6].

It is also report that the annealing process improves the performance properties the TiO_2 [7]. It causes the increases vacancies and due to the movement of the O_2 vacancies [3, 7].

The scope of study for this work is fabricating device with RF magnetron sputtering with different time plasma treatment: 5, 10 and 15 minutes. Furthermore, this paper is study the I-V hysteresis before and after annealing process.

II. METHODOLOGY

We have fabricated memristor using TiO_2 as thin film. The memristive behavior depends on the oxygen vacancies as report earlier [1-3]. The plasma treatment created the TiO_{2-x} to generate the oxygen vacancies.

Overall of this work can be summarized at one flow chart. Fig. 2 show flow chart present summarizes all work.

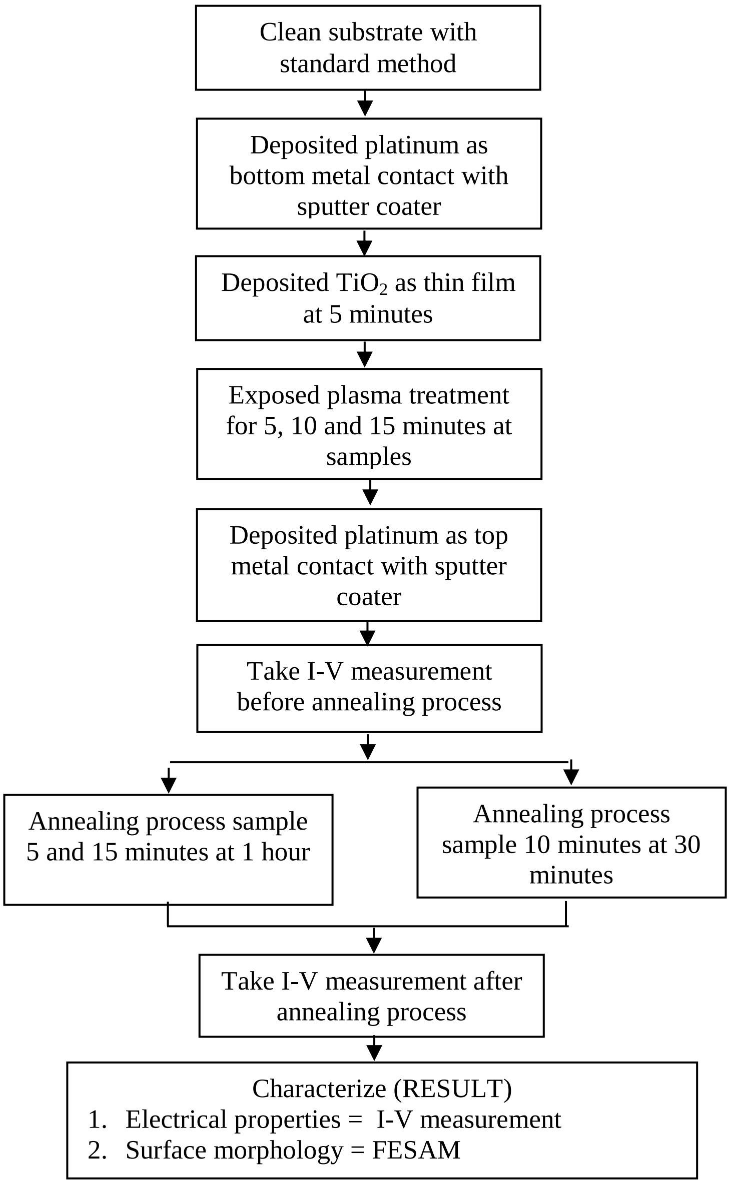


Fig. 1 Flow Chart of work

A. *Bottom and top metal contact deposition by sputter coater.*

First, the glass or substrate was clean with standard cleaning process. We have to deposit the platinum on glass substrate using sputter coater. Platinum (Pt) act as bottom metal contact. The Argon gas was used to accelerate and bombarded the target Pt in vacuum condition. All of this process was done for four minute, with pressure 5mTorr. The Platinum metal contact thicknesses are 60nm.

After the TiO_2 was deposited at top of bottom layer, we introduce the second metal Pt. We had used mask to cover the unwanted area on TiO_2.

B. *Tatinium oxide layer.*

As second layer we have to fabricate the device with TiO_2. At this part we fabricate the layer using RF magnetron sputtering. RF magnetron sputtering is the method to produce the TiO_2 layer. The sample with bottom layer platinum was prepared to load lock chamber before insert to the main chamber.

The sample in chamber was introduced to the argon gas at pressure 5 mTorr. In order to remove the contamination, we have to do pre-sputter before the TiO_2 was fabricated. The structures of device are shows in fig. 2.

Below in table 1 are shows the recipe sputter conditions on the TiO_2 deposition.

TABLE I. SPUTTERING CONDITION.

$Ar:O_2$	50:1 (sccm)
Pressure	5mT
RF Power	300W
Presputter	300s
Process Time	300s
Plsma treatment	300s, 600s, 900s
Target	TiO_2
substrate	Glass

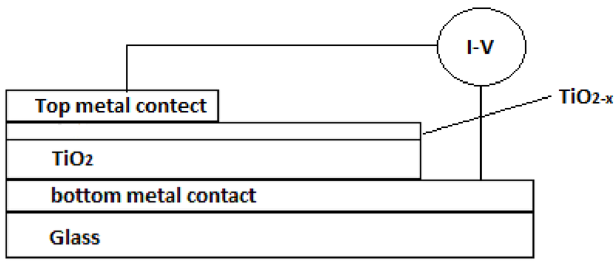


Fig. 2 Structure of device.

C. *Annealing prosess.*

For the annealing process, the temperature used was 450^0C. The 5 minutes and the 15 minutes plasma treatment sample were heated for 1 hour. Meanwhile the 10 minutes plasma treatment sample was heated for 30 minutes.

After the I-V measurement, we were doing the annealing process. In this experiment, we use temperature at 450^oC at

1 hour for sample 5 minutes and 15 minutes. For sample 10 minutes plasma treatment, the temperature is 450°C at 30 minute. The first I-V measurement was taken, the memristive behavior are poor. The result after annealing process will make better the memristive behavior as we see at figure 5(a), (b) and (c).

TABLE II. ANNEALING CONDITIONS.

Parameter	Plasma Treatment		
	5 minutes	10 minutes	15 minutes
Temperature (°C)	450	450	450
Time	1 hour	30 minutes	1 hour

D. *Plasma Treatment.*

Plasma treatment was conducted under the same environment as we deposited the TiO_2 thin film where sputtering process the sample was covered. With this process, the sample was covered with a shutter. With this there are no TiO_2 deposited on the thin film, but the surface of thin film are treated indirectly during the process.

E. *Characterization*

The memristive behavior was measure using the current-voltage (I-V) measurement was taking in loop 0V to -5V, -5V to 5V and 5V to 0V. And the cross section images of memristor are taking from Field Emission Scanning Electron Microscope (FESEM, JEOL JSM 7600F). HOBIRA Jobin Yvon (HR800) Raman Spectrometer is to analyze the phase of TiO_2 phase.

III. RESULT AND DISCUSSION.

The result of this experiment has two sections. The I-V measurements of the sample are taken before annealing and after annealing process.

A. *Part 1: Before anneling process.*

The result I-V measurement was taken at 0V to -5V, -5V to 5V and 5V to 0V for all samples. Figs. 2 (a), (b) and (c) shows that the device 5, 10 and 15 minute plasma treatments before annealing process respectively. We see in Figs. 2 (a), (b) and (c) shows the less I-V hysteresis memristive behavior. Plasma treatments create more damage at the surface and remove the oxygen atoms. And clearly that, the increment plasma treatment time gives the different measurement.

The oxygen concentration for samples 5 minutes, 10 minutes and 15 minutes is 71.8 wt%, 69.74 wt% and 68.63 wt% respectively [10]. There more oxygen concentration removes due to time plasma treatment and create TiO_{2-x} layer. For samples 5 and 10 minutes, shows that improvement memristive behavior. It is because the oxygen concentration decreases from 71.8 wt% to 69.74 wt%. it is become better in 15 minute cause the less oxygen concentration.

The observation done during the experiment, the time increment of plasma treatment is proportional to decreases oxygen concentration. The memristive behavior becomes better if more the plasma treatment time taken.

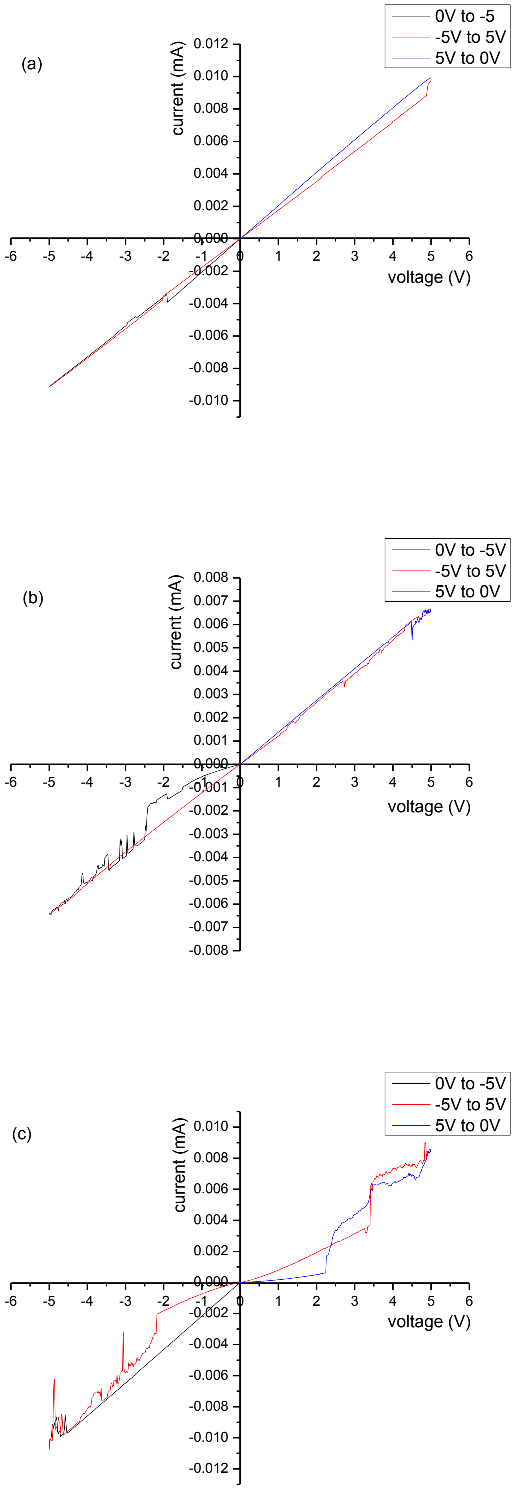


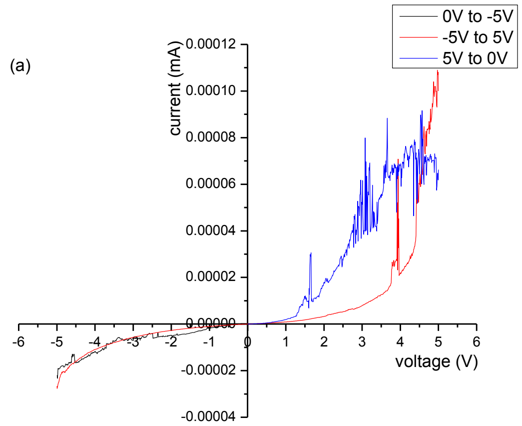
Fig 2 I-V measurement of the devices having TiO_2 layers treated by plasma a) 5 minutes b) 10 minutes c)15 minutes

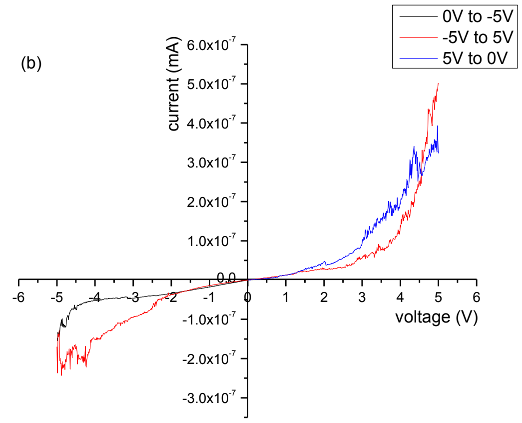
B. Part 2: After annealing process.

Before the annealing process the memristve behavior is very poor. To improve the memristive behavior, we attempt to anneal the device. This is because we assume that annealing can remove oxygen from the TiO_2 layer and more oxygen vacancies result in better memristive behavior.

The annealing process is to expose the device at high temperature [7, 11]. After we have doing the annealing process, the result was change. The memristive increase we will see the differences between them from I-V measurement result as we see in figure 3(a), (b) and (c).

As we see the graph has noise. It is because the heated have damage structure on the surface of TiO_2. Before annealing process, the graph is different there is no noise cause the structure TiO_2 surface is solid. However, the TiO_{2-x} layer increases the oxygen vacancies effect on annealing process [7, 11, 15]. It is causing the memristive behavior better [13].





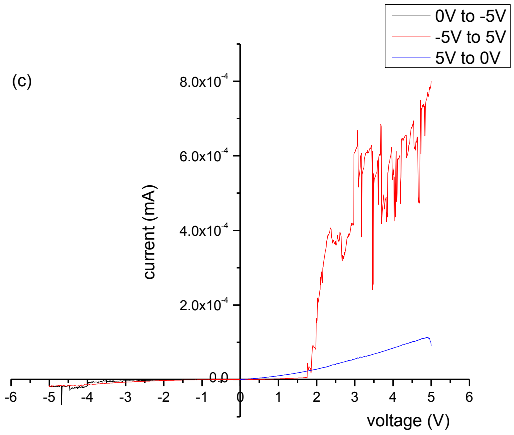


Fig 3 I-V measurement of devices done with annealing at sample a) 5 minutes b) 10 minutes c) 15 minutes

Mostly the performance of TiO_2 depends on its surface properties and surface phase [8]. The TiO_2 exists in three natural phase. They are rutile, anatase and brookite [9].

Figs 4 are shows Raman spectra of samples 5, 10 and 15 minutes plasma treatment after annealing process. Fig. 4 the Raman spectra obtain from the three samples: 5 minute, 10 minute, and 15 minute. At first peak all sample have peak 157 cm^{-1}, 163 cm^{-1}, and 156 cm^{-1}. The second sample peak is 307 cm^{-1} and 256 cm^{-1} for sample 10 minute and 5 minutes respectively. There is no peak at 15 minute. Then the sample has peak 431 cm^{-1}, 403 cm^{-1} and 405 cm^{-1} for sample 5 minute, 10 minute, and 15 minute respectively. Peak 15 minute has peak 832 cm^{-1} but sample 10 and 5 minute has no peak.

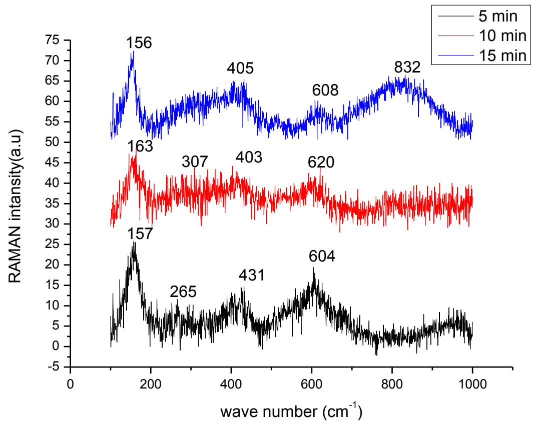
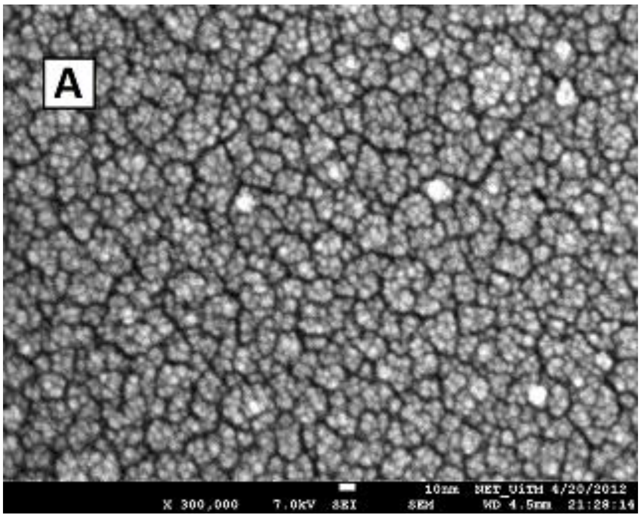
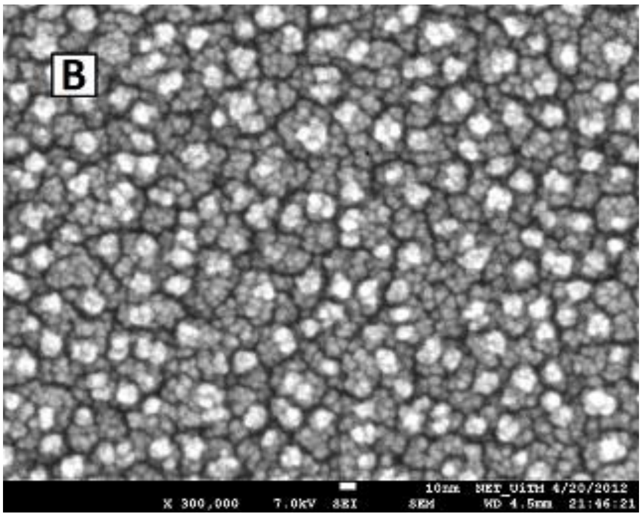
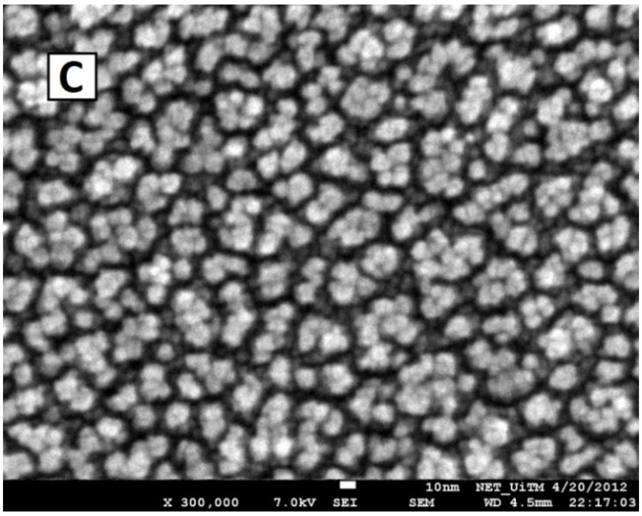


Fig. 4 Raman spectrum for 5 minute, 10 minute, and 15 minute plasma treatment.

The figure 5 shows that the surface layer treated by plasma treatment. In observation the surface below 10 minute treatment time, the particles are agglomerated. The increase the agglomerations cluster when the plasma treatment time up to 10 minutes. The particles clusters become smaller at plasma treatment 15 minutes.







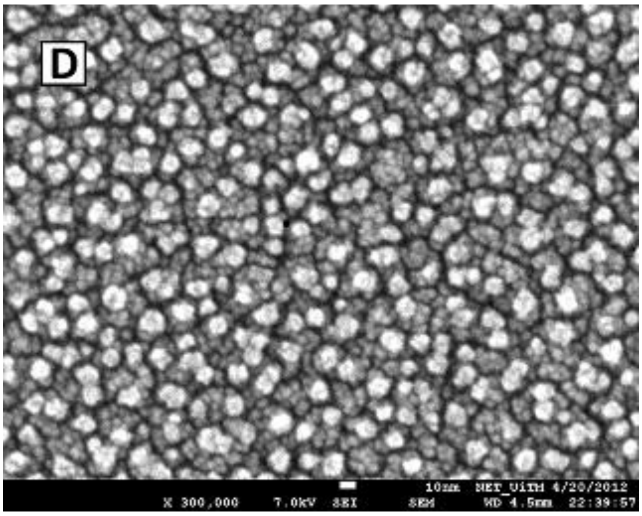
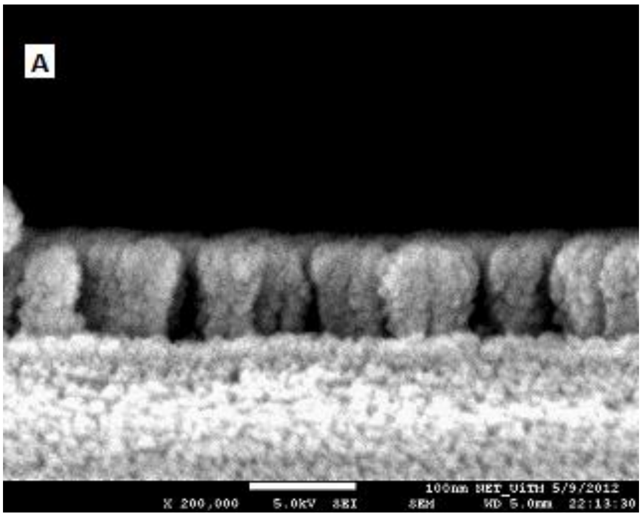
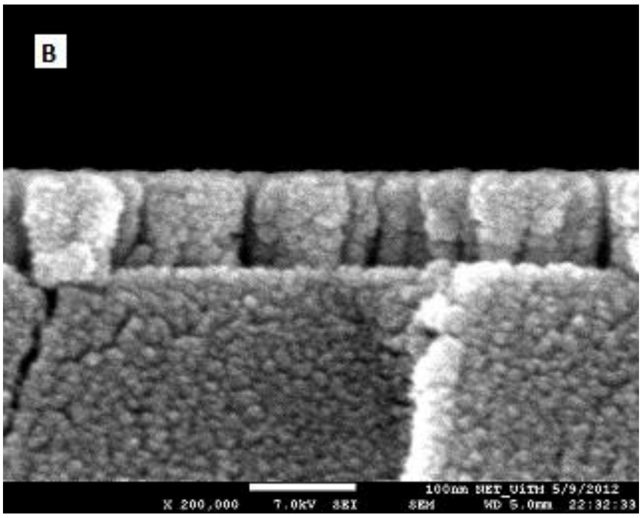
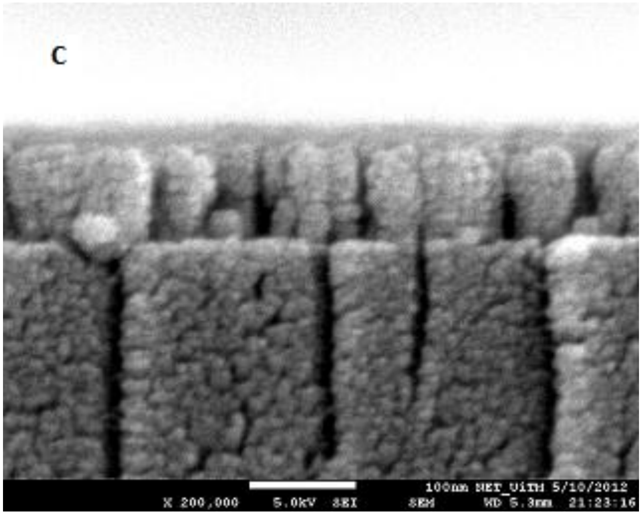


Fig 5 FESEM image surface due to plasma treatment (a) 0 minute b) 5 minutes c) 10 minutes d) 15 minutes treatment adopted from [10].







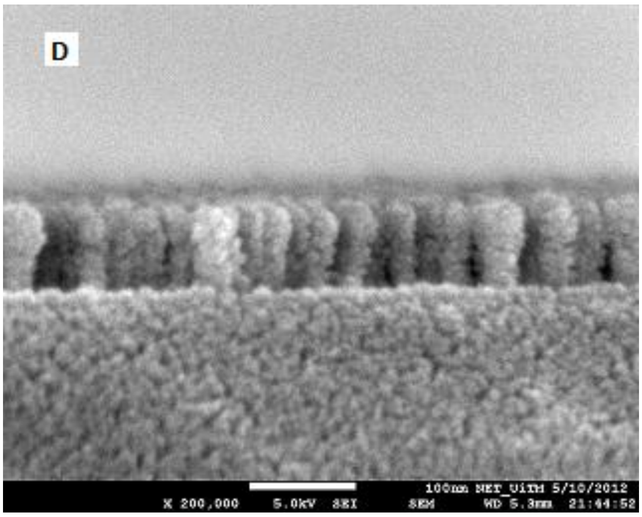


Fig 6 FESEM cross section image due to plasma treatment for sample a) 0 minute b) 5 minutes c) 10 minutes d) 15 minutes adopted from [10].

Fig. 8 shows the cross section the sample. The time plasma treatment taken is relating the thickness TiO_2 layer [10]. The much longer time taken plasma treatment may reduce thin film thickness. We can estimate from figure the thickness more thin if time plasma treatment increase. The improvement memristive behavior, when thin film is thin.

IV. CONCLUSION.

In this experiment we succeed fabricate memristor with different plasma treatment time. The plasma treatment is creating by damage the upper layer (TiO_{2-x} layer). We have found that the thickness of plasma treatment has influence the memristive behavior. The best device has found at 10 and 15 minutes plasma treatment. Much longer time plasma treatment makes TiO_{2-x} layer and cause the better memristive behavior. These results are change after we have done with annealing process. The annealing creates more oxygen vacancies in upper layer TiO_2. The memristive hysteresis has shown the changing after the annealing process. Base on experiment, we conclude that 15 plasma treatments have been damage giving bad particle and not improving the I-V hysteresis. In future, we will test and how to improve the 10 minutes plasma treatment.

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