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Investigation of resistive switching in Anodized titanium Dioxide thin films

A. Saraei, M.J. Eshraghi*, A. Massoudi

Department of Semiconductors, Materials and Energy Research Center, Karaj, Iran

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ABSTRACT

In this work, TiO_2 nanostructures were grown on Titanium thin films by electrochemical anodizing method. The bipolar resistive switching effect has been observed in $Pt/TiO_2/Ti$ device. Resistive switching characteristics indicate that the porous TiO_2 are one of the potential materials for nonvolatile memory applications. Increasing anodizing duration will increase pore lengths which in turn causes increase in high resistance and low resistance differences.

1. INTRODUCTION

Hickmott reported resistive switching phenomenon firstly in some binary oxides in 1962 [1]. Since then, resistive switching phenomenon by electric field application has been reported in many materials [2, 3]. A large variety of materials have shown resistive switching behaviour, including complex perovskite oxides, amorphous silicon, amorphous carbon and organic materials [4]. Binary metal oxides in comparison with ternary and complex metal oxides have better conditions, due to their simple composition and suitable compatibility with semiconductor technology [5]. This phenomenon will be used in information storage and processing instruments, such as Resistive Random Access Memories (RRAM), reconfigurable logic circuits and artificial neuromorphic networks. The switching between High-Resistance State (HRS) and Low-Resistance State (LRS) usually involves oxygen vacancies and metal ions. This will result in defect formation or composition modulation of the active switching region, called Conductive Filament (CF) [6] as shown in Figure 1. The resistive memory stores the information through two different resistance levels: LRS and HRS. The device is simply constructed by sandwiching an oxide material between two metals, called the Metal–Insulator–Metal (MIM) structure. Metals can either be the same (usually inactive) or different (one is inactive and the other is active) materials [7]. A resistance decrease is called a SET or ON switching operation and an increase is called a RESET or OFF switching operation. Some oxides can be switched ON and OFF by applying the same voltage polarity which is called unipolar and others require opposite polarities for ON and OFF switching which is called bipolar. Observation of this behaviour starts by electroforming at the first step, which is frequently created by initial switching from a highly resistive state. Electroforming phenomenon is achieved by applying a voltage larger than set and reset voltages [8]. Titanium dioxide conductivity rises by increasing the temperature due to the oxygen losses and fall of Titanium ions between the vacancies [9]. In addition, Titanium dioxide porous arrays have uniform morphologies, oriented pores and large surface areas with controllable pore sizes that make them attractive for resistive switching devices. Several methods have been used to synthesize porous TiO_2, including hydrothermal, sol gel and electrochemical anodizing. Among these methods, electrochemical anodizing of titanium has attracted the greatest interest, since it can produce self-organized structures at low temperature. In this research we report switching behaviour in anodized Titanium dioxide on Titanium thin films in various anodizing durations. In this paper we investigate resistive switching behaviour of template free anodized porous TiO_2 grown on Titanium thin films. Particularly the effect of anodizing duration on switching behaviour through controlling pores length has been investigated. In many applications, especially in semiconductor device fabrication, whole device are manufactured on silicon or

*Corresponding Author's Email: m.eshraghi@merc.ac.ir (M.J. Eshraghi)

SiO_2 substrate, therefore investigation of switching behaviour of porous TiO_2 grown on Ti thin films deposited on glass substrate is of great importance regarding compatibility with industrial processes.

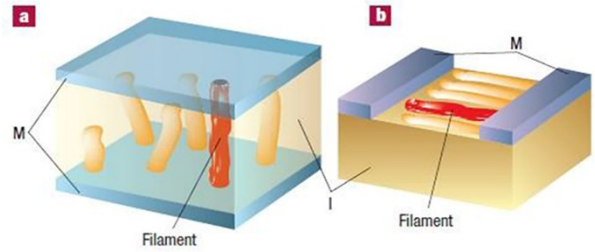

Figure 1. (Adapted from Ref. [6]) Filamentary conduction of RRAM in (a) vertical, and (b) lateral configurations.

2. EXPERIMENTAL PROCEDURES

Titanium thin films (300 nm in thickness) were deposited by RF magnetron sputtering on glass substrate at room temperature and cathode power of 250 W. The base pressure and working pressure was 4×10^{-5} mbar and 3×10^{-3} mbar, respectively. Titanium sheet with 99.8% purity (BDH, England), 3 inches in diameter was used as the target material source. Before using as sputtering target, the sheet was cleaned by sonication in methanol, acetone, and deionized water for 20 minutes. As-Deposited thin films have been used for anodizing in 0.5% HF solution. The anodizing potential was kept constant at 5 V. The specimen was placed as the anode in the electrochemical cell, with a platinum cathode. The distance between the specimen and platinum was kept at 2 cm. For each anodizing process, 1.5 cm^2 of the specimen surface was exposed to the electrolyte solution. The HF concentration was kept constant in all experiments to obtain the nanostructures. Several samples with same anodizing conditions have been anodized with different anodizing durations (2, 4 and 6 minutes). After anodizing, the samples were immediately rinsed with deionized water and dried with nitrogen gas. The crystal structure of TiO_2 nanostructure sample was confirmed by X-ray Diffraction (XRD) with Cu kα radiation (λ=0.154 nm). Field Emission Scanning Electron Microscope (FE-SEM Mira3-XMU) was used to characterize the nanostructures. The platinum electrodes (100 nm in thickness) were deposited by RF sputtering on porous TiO_2 at room temperature and base vacuum of 3×10^{-4} mbar. The samples were then annealed in Nitrogen atmosphere and at 250ºC for 30 minutes. The Keithly 2400 source-meter connected to a probe station was used to obtain I-V curves of the sample and characterizing the switching behaviour. Titanium at the bottom has been connected as the anode electrode and platinum on the top has been connected as the cathode electrode.

3. RESULT AND DISCUSSION

Titanium dioxide nanostructure was grown by anodizing. To examine the effect of anodizing duration on the pores formation, the anodic oxidation of Titanium was carried out at 0.5 % HF concentration with different reaction times. Figure 2. shows the XRD pattern of the TiO_2 nanostructure prepared by anodizing method for 2, 4 and 6 minutes. It is obvious that the (103) and (301) diffraction peaks of the as-prepared TiO_2 can be observed at around 36.76° and 77.98° which are corresponding to tetragonal crystal structure of anatase phase (Ref. cod 01-071-1168) in the sample anodized for 2 minutes. For the sample anodized for 4 minutes, (101) and (202) diffraction peaks of as-prepared TiO_2 can be observed at around 36.60° and 77.84° which are corresponding to tetragonal crystal structure of rutile phase (Ref. cod 01-088-1174). For sample anodized for 6 minutes, (101) and (202) diffraction peaks of the as-prepared TiO_2 can be observed at around 36.74° and 77.66° which are specific to tetragonal crystal structure of rutile phase (Ref. cod 01-088-1174). In addition, lattice parameters are estimated by the Bragg equation which are in good agreement with reference card values and lattice strains are evaluated by the Williamson Hall method (Table 1). It can be seen that by increasing the anodizing duration from 2 to 6 minutes, crystallite size increases from about 4 nm to 17 nm. FE-SEM images of the samples anodized for 2, 4 and 6 minutes are shown in Figure 3(a-c). As it can be seen, increasing the anodizing duration has had little effect on the size of the pores. The porous structure formed at different anodizing durations show diverse morphologies [9]. As anodizing duration increased, the nanostructure showed a pore network. Large anodizing durations resulted in merged pores (Figure 3(c)). The diameters of the pores grown in 2, 4 and 6 minutes were 9.7 nm, 10.9 nm and 12.01 nm, respectively. All anodized samples were used for examining the resistive switching behaviour.

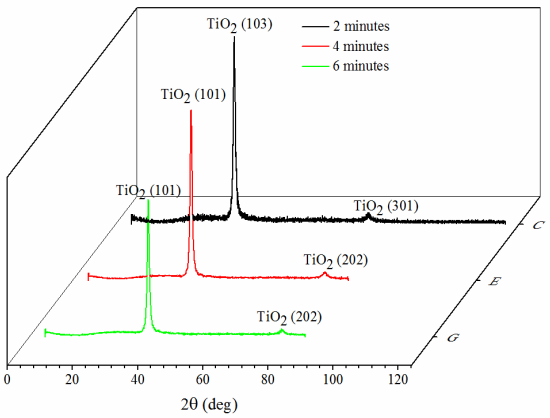

Figure 2. XRD patterns of the TiO_2 nanostructured samples anodized for 2, 4 and 6 minutes.

TABLE 1. Lattice parameters of the samples anodized for 2, 4 and 6 minutes.

Anodizing time	a(Å)	b(Å)	c(Å)	Crystallite size (nm)	Lattice strain (%)
2 minutes	3.73	3.73	9.88	4.4	2.48
4 minutes	4.52	4.52	2.90	11.2	0.98
6 minutes	4.39	4.39	2.89	17.4	0.63

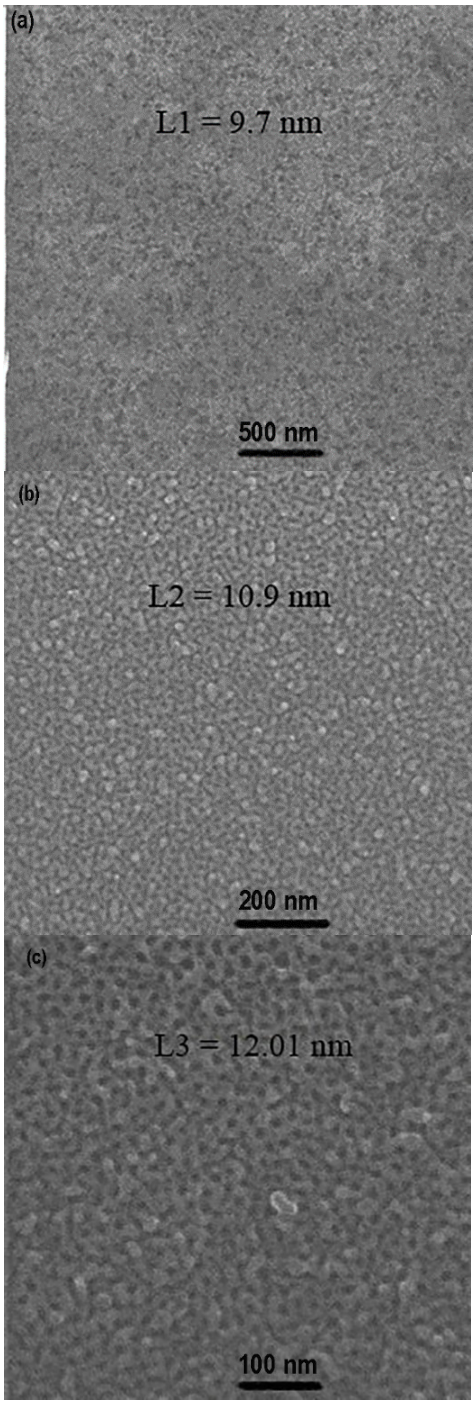

Figure 3. SEM images of Titanium dioxide structure anodized for (a) 2 ,(b) 4 , and (c) 6 minutes.

Figure 4. shows resistive switching behaviour from LRS to HRS (Reset) in the samples anodized for 2, 4 and 6 minutes. Reset Voltages are measured as 10.3V, 6.67V and 6.1V for the samples anodized for 2, 4 and 6 minutes, respectively. Before the switching test, a forming voltage of 20 V with 300 mA current limits has been applied for characterizing switching behaviour. Sweeping voltage from 0V to 11V applied for diagnosing LRS to HRS state. In the sample anodized for 2 minutes, by increasing bias voltage up to 10.3V the resistance decreased to 2.43KΩ and after that it tended to increase. For the sample anodized for 4 minutes, by increasing the bias voltage up to 6.67V, resistance decreased down to 0.72KΩ and then by increasing the bias voltage, it tended to increase which shows that reset voltage for this sample is around 6.67V. In the sample anodized for 6 minutes, by increasing bias voltage to 6.1V, the resistance decreased to 0.31KΩ. Further increase in voltage showed increase in resistance which is the evidence of resistance switching. Figure 5. shows resistive switching behavior from HRS to LRS (Set) for the samples anodized for 2, 4 and 6 minutes. Set voltages are measured as -9.11V,-7.51V and -6.89V for the samples anodized for 2, 4 and 6 minutes, respectively. High resistances reaches 3.21KΩ, 3.95KΩ and 4.22KΩ for the samples anodized for 2, 4 and 6 minutes, respectively, which are in accordance with crystallite sizes of 4, 11 and 17nm.

At the Set voltage and by increasing the voltage amplitude, the resistance values decreased. The structure acts as a bipolar resistive switching, Polarizations with approximately equal voltages. The bipolar resistive switching device structure is usually asymmetric because in this structure different materials are used as top and bottom electrodes. This is an example of anion migration and oxygen vacancies which typically have a higher mobility than cations according to [10]. Bipolar switching behaviour happens in transition metal oxides because of oxygen vacancy defects [11]. This resistance change shows the resistive switching behavior which acts between two high resistance and low resistance states and is characteristic of a resistive memory. because the set and reset voltages are in opposite Oxygen vacancies move toward metal electrodes because of applied electrical field during the switching operation. We expect that TiO_2/Ti junction plays a basic role in the hysteretic I-V behavior. Structure performance can be optimized by involving metal ion doping, nano-dot embedding in the oxide layer, applying a compliance current or decreasing the oxide layer thickness [13]. Comparison of resistive switching characteristic of the different samples shows that longer pores produced by increased anodizing duration, have larger resistance difference between LRS and HRS states.

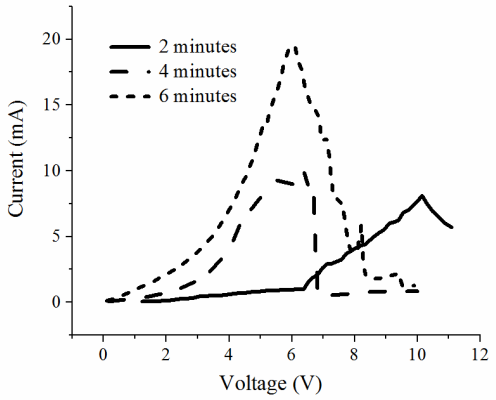

Figure 4. Reset process of the anodized samples.

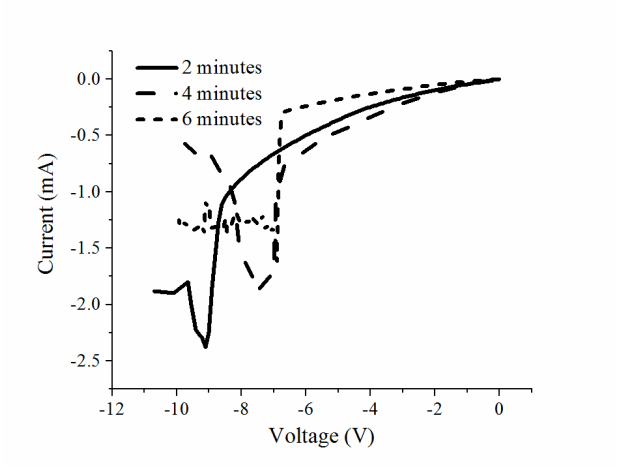

Figure 5. Set process of the anodized samples.

4. CONCLUSION

Porous Titanium dioxide has been prepared on Titanium thin films by anodization method. Bipolar resistive switching behavior in $Pt/TiO_2/Ti$ Structure has been investigated. In the samples anodized for 2, 4 and 6minutes pores with diameters of 9.7, 10.9 and 12.01nm were formed. The crystallite size of the samples increased from 4 to 17 nm by increasing anodizing time from 2 to 6 minutes which is in accordance with high resistance resistivity values of 3.21, 3.95 and 4.22kΩ, respectively. Reset Voltages are measured to be 10.3, 6.67 and 6.1V for the samples anodized for 2, 4 and 6 minutes, respectively. Switching from HRS to LRS state and from LRS to HRS has been observed and increase in anodizing timeaccompanied with increase in difference of resistance in two LRS and HRS states.

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