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Resistive switching and impedance characteristics of M/TiO_{2-x}/TiO_2/M nano-ionic memristor

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ABSTRACT

Employing electrochemical impedance spectroscopy (EIS), we demonstrate a novel approach towards characterizing the switching behavior of nano-ionic memristor, M/TiO_{2-x}/TiO_2/M where M = Au, fabricated using combined RF/DC magnetron sputtering techniques. The non-linear resistive switching behavior of the device has been investigated using a constant potential sweep technique to observe *I-V* switching profile (a pinched hysteresis loop) in which ex-situ impedance response has been measured by interrupting the potential sweep ($mV\,s^{-1}$) over different distinct regimes (pristine device, SET and after zero-crossing). Accordingly, the obtained EIS spectra are corroborated with oxide circuit model and the corresponding numerical fittings of the impedance response reveals distinct RC frequency domains as exemplified in the equivalent circuit models obtained using the simulated impedance response and attributed to the interfacial barrier between the stoichiometric and non-stoichiometric TiO_2 respectively. It is evident that the device shows various functional features as memory element owing to the transport of mobile charges in TiO_{2-x} when the bias potential (V) is applied across the device. It is revealed that EIS studies render a new insight into much acclaimed formation and annihilation of nanofilament like dendrites (magneli phase of titania, Ti_nO_{2n-1}) which are found to be responsible for the change of switching states between low resistance state (LRS) and high resistance state (HRS) respectively. In order to validate the memory retention and endurance characteristics, the reproducible resistive switching is found to occur consistently over 10^4 s and the device endurance has been verified by toggling between HRS and LRS over 1000 cycles.

1. Introduction

In 2008, the existence of fourth missing element called "Memristor" which relates charge (q) and flux (ϕ) has been discovered although the conceptual thought was put forth by Chua in 1971 [1,2]. The new element of surprise fills the missing gap existed between the well-known passive electronic components viz., resistor (R), capacitor (C) and inductor (L). It exhibits several functional features as memory element invoking the transport of ionic charges in solid state constituted by the applied electrical flux. The movement of charge (q) transport directly corroborates with memory characteristics owing to the stability of migrated charges when the applied potential is removed. Such property is construed as non-volatile in nature and correlated with resistive random access memory (Re-RAM). Thus, a new modern solid state memory was born which operates solely on the change of resistance state [3]. Memristor is regarded as a two terminal passive having metal/oxide/metal structure in which oxide layer is sandwiched between the top and bottom metal electrodes [4,5]. Pragmatically, the first memristor device was reported in the year 2008 by HP labs, in which titanium dioxide layer is sandwiched between the top and bottom platinum blocking electrodes [4]. The underlying technical merit centered on memristor is that the manipulation of solid state motion of ions between the two blocking metal electrodes. This breakthrough paved the way for a new class of memories which can perform much different functionality in digital, analog and universal memory applications [6–11]. Conventional technologies such as static random access memory (SRAM) and dynamic random access memory (DRAM) have already reached their scaling limits and many other emerging memory technologies are proposed as alternative memory technologies, for instance magneto resistive random access memories (MRAM) and Phase change random access memory (PCRAM) [12–14]. Among them ReRAM scores high in terms of scalability, switching speed and ease of fabrication [12]. The only impediment that has restricted memristor from being marketable is the lack of proper

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understanding of intrinsic switching mechanism. The switching mechanism in memristor is attributed to the variation in ionic, electronic and thermal properties [15]. Although, there are ample reports on switching mechanism of memristor, but till date none of the mechanisms are elucidated, rather they are suggested on the basis of theoretical understanding and/or with the aid of advanced physical and electrical characterization techniques [15,16]. The physics involved underneath the resistive switching operation in titanium dioxide based memristor is perceived as being one of the following: (i) the formation and rupturing of conducting filaments (kind of dendrites) originated from BE [17–22], and (ii) electrical trap related process [22–24]. Recently, resistive switching characteristics of two different device structures viz., Pt/TiO_2/Pt and Pt/TiO_{2+x}/TiO_2/Pt were studied by Lee et al. and Qingjiang et al. respectively using electrochemical impedance spectroscopy (EIS) [24,25]. Nevertheless, to the best of our knowledge, Au/TiO_{2-x}/TiO_2/Au has not been studied using EIS technique hither to and a detailed elucidation is still missing.

EIS is a powerful technique to study the processes occurring in any electrochemical couple. In the present investigation a two electrode contacts are made of gold bottom and top electrode sandwiched with a two layer ion permeable titania nano thinfilm layers acting as memristor and it is expected that such memristors undergo resistive switching manifested by its ion migration. A small sinusoidal perturbation (potential or current) of fixed frequency is applied across the device under test (DUT) to measure the phase and the magnitude of the resulting current (potential) [26]. Strukov et al. proposed a physical model of a two-terminal electrical device that behaves like a perfect memristor in order to define the change in resistance state of it [4]. Although potentiodynamic EIS is performed by Greenlee et al. in $LiNbO_2$ based analog memristor but it does not clearly define the SET and RESET operation occurring in it [27,28]. In the present work, we report our new interpretation invoking data obtained from EIS technique and studied the switching characteristics which comprehensively shed light into widely accepted filamentary conduction mechanism in order to explain the resistive switching between SET and RESET of Au/TiO_{2-x}/TiO_2/Au memristor. All these impedance interpretation are supported by the simulating the impedance data using genetic algorithms (theoretical fitting) yielding the equivalent circuit models corresponding to the stable switching states of the memristor fabricated in the present work.

2. Materials and methods

Initially p-type silicon is taken as substrate on to which 335 nm SiO_2 is deposited from a Si target by using RF sputtering technique by maintaining the base pressure of 1.76×10^{-6} mbar. It is important that the base pressure of the order of 10^{-6} mbar is maintained during the entire process of deposition. The reason for coating SiO_2 is to eliminate the semiconducting effect of silicon substrate. A 15 nm Ti layer is deposited on to SiO_2 layer that became a seed layer for the growth of Au bottom electrode (BE). Pictorial representation of the stack structure is shown in Fig. 1.

The bottom contact is made by sputtering a gold bottom layer (30 nm) on to Ti layer (being used to facilitate the good adhesion) using DC magnetron sputtering. Shadow Mask #1 is placed on it meticulously (care must be exercised to minimize the shadow effect) so that a portion of the bottom contact can be kept isolated from titanium dioxide layer. A 55 nm stoichiometric TiO_2 layer is deposited on to Au layer using a Ti target in the presence of flowing Ar/O_2 gas mixture following the conditions described in Table 1 while maintaining the substrate temperature at 300 °C for an optimized deposition. Further, a 92 nm TiO_{2-x} non-stoichiometric layer is deposited by employing RF sputtering technique by using a Ti target. A suitable chamber partial pressure (Ar/O_2: 85/15%) was maintained (preferably at 9.8 mTorr). Again to complete the bilayer structure, gold top electrode was deposited following the above described procedure for sputtering BE contact. It is well known that Au and Pt are inert and ion blocking electrodes (in the present case it is O^{2-}). Moreover, Au exhibits advantages like lower cost and low work function (5.1 eV) compared to Pt (6.35 eV). The RF/DC magnetron sputtering is performed employing a sputtering system (Plassys-300, France). Our fabricated memristor device is basically circular in shape. That is, region corresponding to TiO_{2-x}/TiO_2 layers are about 3 mm in diameter. While the top gold electrode is of rectangular in shape whose dimension is 1 mm × 1 mm.

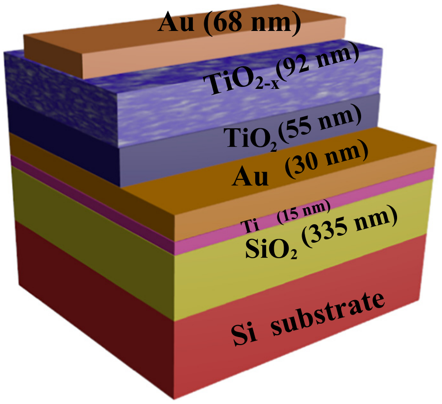

Fig. 1. The 3-D stack structure of Au/TiO_{2-x}/TiO_{2-x}/Au based memristor.

Table 1
Deposition parameters for the Au/TiO_{2-x}/TiO_2/Au memristor during the process of fabrication.

Material	Power (W)	Working pressure (mTorr)	p_{O2} (sccm)	p_{Ar} (sccm)	Substrate temperature (°C)
SiO_2	70	10.3	4	12	RT
Ti	100	8	–	12	RT
Au	–	8.3	–	12	RT
TiO_2	100	10.4	3	12	300
TiO_{2-x}	100	9.8	2	12	300

The various control parameters involved in the process of fabrication is illustrated in Table 1. X-ray diffraction (XRD) patterns on the coated films were collected on Rigaku powder diffractometer (SmartLab® high-resolution X-ray diffractometer equipped with SmartLab Guidance software) 2θ range from 20° to 80° angle using CuKα radiation. Ex-situ HRSEM characterization was obtained at an accelerating voltage of 5 kV employing a Hitachi S-4800 High Resolution Scanning Electron Microscopy equipped with Energy Dispersive Spectrometer (EDX). Ex-situ EIS measurement is performed using Wonatech Electrochemical workstation MP3 equipped with Zive lab software for data acquisition (South Korea) at zero bias condition. All these measurements are obtained at room temperature. Further, the resistive switching characteristics and other memory parameters such as endurance and retention time were carried out by using ArcOne Memristor characterization system equipped with FPGA hardware setup and dedicated software for data acquisition and a graphical user interface (GUI). The latter system is regarded as a standard instrument for characterizing memristors and other two terminal emerging memories. The set-up extends a 32 × 32 crossbar memory array [29,30]. A homemade two probe setup is employed to perform the measurements by connecting the TE contact and BE contact to Bit line and Word line respectively.

3. Physical characterization

3.1. XRD

Fig. 2 shows the indexed XRD patterns corresponding to