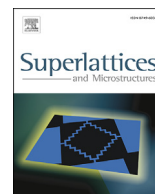




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Resistive switching in microscale anodic titanium dioxide-based memristors

V. Aglieri ^a, A. Zaffora ^a, G. Lullo ^a, M. Santamaria ^c, F. Di Franco ^c, U. Lo Cicero ^b, M. Mosca ^a, R. Macaluso ^{a,*}^a Thin Films Laboratory (TFL), Dipartimento di Energia, Ingegneria dell'Informazione e modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze (ed. 9), 90128, Palermo, Italy^b Osservatorio Astronomico di Palermo, Istituto Nazionale di Astrofisica (INAF), Via Ingrassia, 31, 90123, Palermo, Italy^c Electrochemical Materials Science Laboratory, Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali (DICAM), Università di Palermo, Viale delle Scienze (ed. 6), 90128, Palermo, Italy

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ABSTRACT

The potentiality of anodic TiO₂ as an oxide material for the realization of resistive switching memory cells has been explored in this paper. Cu/anodic-TiO₂/Ti memristors of different sizes, ranging from 1 × 1 μm² to 10 × 10 μm² have been fabricated and characterized. The oxide films were grown by anodizing Ti films, using three different process conditions. Measured IV curves have shown similar asymmetric bipolar hysteresis behaviors in all the tested devices, with a gradual switching from the high resistance state to the low resistance state and vice versa, and a R_{OFF}/R_{ON} ratio of 80 for the thickest oxide film devices.

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1. Introduction

Memristors are metal/insulator/metal devices whose resistance can be varied by applying an electrical field between the two metal contacts. The fingerprint of this behavior is visible through a non linear current-voltage characteristic which is normally represented by an hysteresis loop [1–3]. This property allows memristors to be employed as non volatile memory devices as well as resistive random access memories (RRAMs) [4]. Moreover, the capability of memristors to sustain multiple resistive states can be also exploited for realizing multi-level memories, programmable analog circuits and neuromorphic logic elements [2], [5]. Because of their simple structure, prone to extreme down scaling, 3-D stacking potentiality, high speed, low power consumption and excellent compatibility with the complementary metal-oxide-semiconductor (CMOS) technology, memristors are rightly considered the elemental bricks for a next generation of high-density nonvolatile memories [3,4].

Typical employed insulator layers are binary metal oxides such as TiO₂ [1,6–8], ZnO [9,10], VO₂ [9], NiO [4], HfO₂ [4], and Ta₂O₅ [4]. Metal oxides are typically rich in defects. When they are inserted in a memristive structure and undergo electrical stresses, they exhibit a change in the electrical resistivity which leads to the two typical resistance switching states of the memristor: the High Resistance State (HRS) or OFF state, and the Low Resistance State (LRS) or ON state. The switching

* Corresponding author.

E-mail address: roberto.macaluso@unipa.it (R. Macaluso).

behavior is dependent not only on the oxide material but also on the metal contact employed, which enables different mechanisms for the conduction within the oxide film. In particular, if the contact metals are both inert (e.g. Pt), the most probable resistive switching mechanism is the formation of conductive filaments within the oxide film [3]. The filaments are formed by oxygen vacancies, already present inside the defective oxide and/or introduced in the layer during the forming step of the device [11], that under electrical stimuli start to migrate, forming conductive paths between the two metal contacts [12]. On the other hand, when non-inert metals (e.g. Cu, Ag) are used as electric contacts, another possible switching mechanism is the formation of metallic bridges [10]. In this case, applying a proper positive voltage to the non-inert metal contact, the metal atoms start to migrate through the oxide as cations and deposit in metallic state at the opposite electrode. When the forming metal bridge reaches the other contact, a conductive path allows the resistance switching of the device, from the HRS to the LRS [13].

Titanium dioxide is nowadays largely used for resistive memory applications because of its abundance in nature and the excellent reported results. The two most common techniques employed for the deposition of TiO₂ films are RF sputtering and atomic layer deposition (ALD): they are, however, both expensive in terms of equipment and power consumption [1,6]. As an alternative, anodizing is a low cost and low power consuming process (it is carried out at room temperature) to grow oxides on valve metals (such as Ti) and valve metals alloys that can be used in electronic devices [14,15]. Furthermore, anodizing is a viable tool to grow oxides whose composition, thickness and structures can be easily tuned by selecting the metallic substrate and the electrochemical conditions (i.e. formation voltage, growth bath) [16]. So far just a few papers have reported memristive behavior of anodic grown TiO₂-based memristors. In particular, Miller et al. [7] have grown the oxide film by applying a constant voltage for different time durations and have fabricated large area memristors by using silver paste as electrical contacts. Diamantiet al. [8] instead have used conductive atomic force microscopy (c-AFM) for studying the homogeneity at the nanoscale of the anodic oxide grown in galvanostatic mode (i.e. by applying a constant current) and have found out a memristive behavior in an AFM tip/Nanocrystal TiO₂/Ti system. Memristive effect has also been found with anodic TiO₂ grown in the form of nanotubes [17].

In this work we expand the previous studies by introducing the dependence of the memristive behavior of micrometric anodic TiO₂-based memristors on the device size as well as on the anodizing parameters.

2. Experimental details

2.1. Fabrication process

All devices have been fabricated following the process steps depicted in Fig. 1. They result in the Cu/anodic-TiO₂/Ti sandwich structure of Fig. 1 (h), with Cu top electrodes of different sizes and a common Ti bottom electrode. The fabrication of

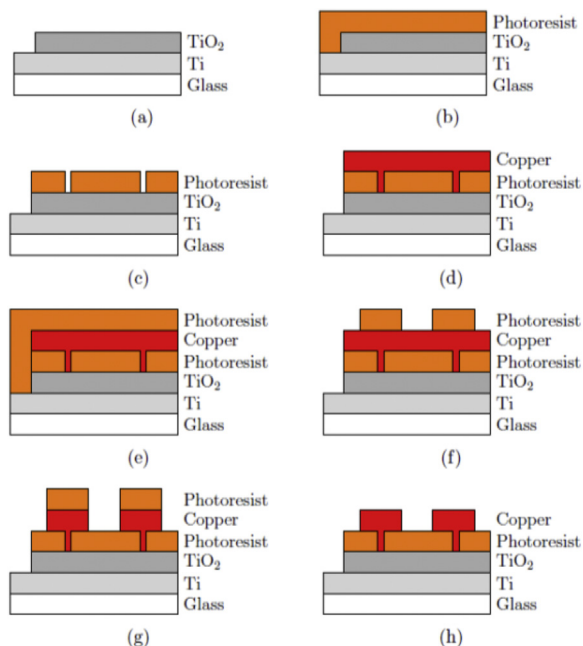


Fig. 1. Process steps for the memristors fabrication. (a) Anodic TiO₂ thin film grown on the metallic Ti film. A large area of Ti is preserved to be used as bottom contact during the electrical measurements. (b) Photoresist spin coating for the definition of the vias. (c) Laser-assisted lithography and vias definition after development. Hard baking of the photoresist. (d) Copper deposition. A metal mask is used to keep clear the Ti bottom electrode. (e) Photoresist spin coating for defining large Cu pads, using the same parameters as in the previous lithographic step. (f) Exposure and developing of the second mask. (g) Copper etching, using a 9 wt% solution of ferric chloride in distilled water for 30 s, to obtain the Cu pads of 500 × 500 μm². (h) Completed devices.

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