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Optimization of Synthesis Protocols to Control the Nanostructure and the Morphology of Metal Oxide Thin Films for Memristive Applications

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Abstract. We propose a multi-technique approach based on in-vacuum synthesis of metal oxides to optimize the memristive properties of devices that use a metal oxide thin film as insulating layer. Pulsed Microplasma Cluster Source (PMCS) is based on supersonic beams seeded by clusters of the metal oxide. Nanocrystalline TiO_2 thin films can be grown at room temperature, controlling the oxide stoichiometry from titanium metal up to a significant oxygen excess. Pulsed Electron beam Deposition (PED) is suitable to grow crystalline thin films on large areas, a step towards producing device arrays with controlled morphology and stoichiometry. Atomic Layer Deposition (ALD) is a powerful technique to grow materials layer-by-layer, finely controlling the chemical and structural properties of the film up to thickness of 50-80 nm. We will present a few examples of metal-insulator-metal structures showing a pinched hysteresis loop in their current-voltage characteristic. The structure, stoichiometry and morphology of the metal oxide layer, either aluminum oxide or titanium dioxide, is investigated by means of scanning electron microscopy (SEM) and by Raman scattering.

INTRODUCTION

The term *memristor* was first introduced in 1971 by L. O. Chua to identify the fourth fundamental passive circuit element, linking charge and magnetic flux [1]. This circuit element is a resistor whose resistance is a function of the charge that has passed through it. Since the state of the memristor depends on its previous history, it is called a *memory-resistor*. Memristance properties have been observed in a wide variety of devices that can be distinguished by identifying the material responsible for the switching behavioror in terms of the switching mechanism or the geometry of the device itself [2,3]. A great number of devices are built in a metal-insulator-metal sandwich structure where the insulating layer is either a thin film of an inorganic compound [2,3], such as a transition metal oxide or a solid electrolyte, or a thin layer of an organic material [4]. Other kinds of memristor include, just to cite a few, those with spin-polarized electrodes [5] and the organic memristor developed by one of us, where the switching behavior is obtained using a conductive polymer, polyaniline, exploiting the significant difference of conductivity in its reduced and oxidized states [6].

These devices have attracted a great interest worldwide because they hold the promise to overcome the present limitations in semiconductor industry in terms of downsizing of transistors on a single chip. More than this, the ability of memristors to “remember” the history of the charge that has passed through them in the past, is very promising for the realization of an hardware analog of a synapse [7].

As a first technological advance these devices are being explored as future fast non-volatile memories, that can be implemented in cross-bar geometries with very high densities of ‘bits’, since a memristor can have a later size of only a few nanometers [8]. A further promising development is the realization of a computing architecture where the ability to perform logical operations and to store the information is achieved by the same device, at variance with what happens today, where the computation is performed by the CPU while the data storage is achieved with either volatile (faster) or non-volatile devices (slower). However, the most ambitious program is the use of such devices to build an hardware analog of the brain, that could help in a variety of tasks, either to simulate a real brain or to perform adaptive learning in order to respond in an active way to the stimuli that, for example, can arrive from a

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network of sensors. In this framework, a part of the research effort is devoted to the development of logical operations that go beyond the usual Boolean logic [9,10].

In the present contribution we will describe several techniques for the deposition of thin films and we will discuss the advantages and disadvantages of the various approaches. We will then concentrate our attention on two oxide materials, aluminum oxide and titanium dioxide, showing a characterization of the film morphology and structure together with the electrical response of the metal-insulator-metal sandwich.

EXPERIMENTAL

The thin films described in the present contribution have been deposited using three different techniques: the Pulsed Microplasma Cluster Source (PMCS), the Pulsed Electron beam Deposition (PED) and the Atomic Layer Deposition (ALD).

The PMCS technique is based on the use of supersonic pulsed beams of clusters of the metal oxide, which deposit at high energy on the substrate, giving rise to a nanostructured thin film where the porosity degree and nanocrystalline structure can be controlled and tuned by changing the deposition parameters, also when the film growth is performed at room temperature.

PED is a deposition technique based on the use of a plasma of the desired material, which is extracted from the target by pulsed electrons. The technique has the advantage of being able to transfer with precision the target composition to the substrate, allowing a precise tuning of the stoichiometry. Furthermore, PED is a fast technique, usually employed for thin film coating or in photovoltaics. However, it is also suitable for the deposition of thin films, when the plasma is appropriately filtered by the unwanted particulate.

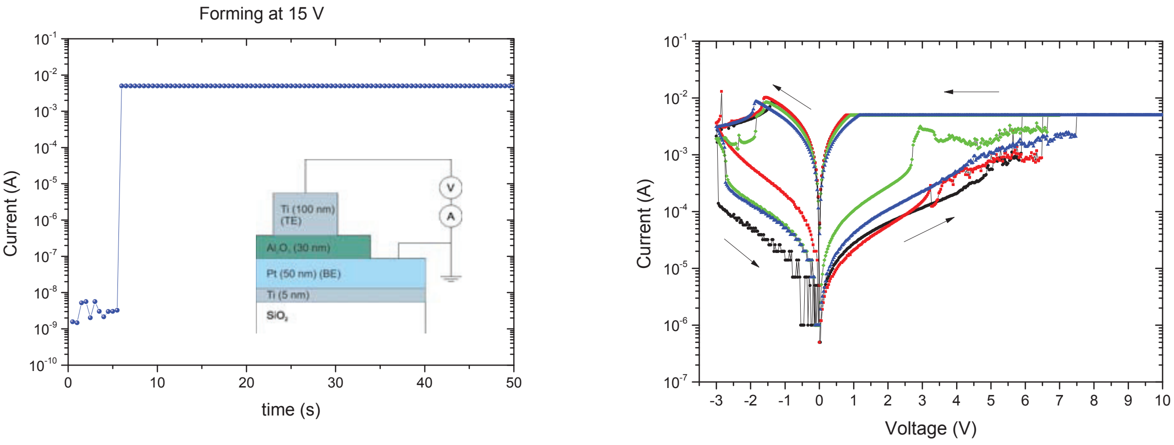
We finally used ALD to obtain an higher control on the film thickness and homogeneity. Moreover, the possibility to obtain conformal coating of nanostructures is an interesting development for future designs in which the memristor will be realized on the nanoscale.

In the following we will present a few examples of metal-insulating-metal sandwiches showing nice pinched hysteresis loops together with an investigation of the morphology and crystallinity of the thin films.

Aluminum Oxide

For this device the metal-insulator-metal structure is composed of Pt, as bottom electrode, a thin film of Al_2O_3 and Ti as top electrode [11]. The substrate is prepared by electron beam evaporation of 5 nm of Ti (adhesion layer) and 50 nm of Pt on an electric fused quartz wafer. The Al_2O_3 thin film is grown by ALD at 270 °C and 60 mbar, using a mixture of He and palladium purified H_2 as a carrier gas. The deposition is performed with 60 ALD cycles to get a nominal thickness of about 30 nm. Raman and X-rays diffraction measurements suggest that the oxide film is amorphous. The metal-insulator-metal structure is obtained depositing a top electrode of Ti, with a thickness of approximately 100 nm, through a shadow mask by an Edwards EB3 Electron Beam Evaporator at a base pressure of 4×10^{-6} mbar. The top electrode has an hexagonal shape with a lateral size of approximately 500 μm. Further details on the sample preparation can be find in ref. [10].

A scheme of the $Pt/Al_2O_3/Ti$ stack is plotted in the inset of Fig. 1a, with the standard two terminal connections, where the bottom electrode is grounded. The device requires an electroforming step, which is obtained applying a positive voltage of 15V on the top electrode for a few seconds. As can be seen in Fig. 1a, the initial resistance of the aluminum oxide film is of the order of a few GΩ, but after a few seconds the current reaches the compliance limit, set at 5 mA. Figure 1b shows a few current-voltage cycles with a nice pinched hysteresis. The curves are, however, not perfectly reproducible from cycle to cycle. The voltage at which the device is set, changing from the OFF to the ON state, varies between roughly 5.5 and 8 V, and the resistance ratio at low voltages is approximately two orders of magnitude.



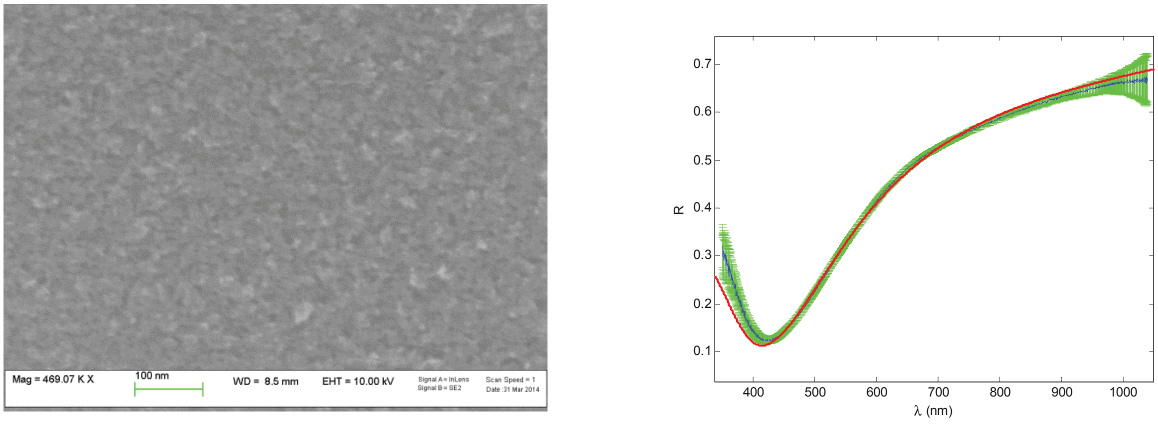
(a)

(b)

FIGURE 1. Electrical response of the Pt/Al_2O_3/Ti stack. Panel a): the forming step is obtained applying a constant positive (on the top electrode) voltage of +15V. In the inset: a scheme of the metal-insulator-metal structure. Panel b): a series of current-voltage cycles. Note that the on the negative voltage side the current is plotted as –I. The arrows indicate the direction of measurement. The cycles are measured at 150 mV/s.

Titanium Dioxide

Titanium dioxide thin films have been prepared both by PMCS and by means of ALD. Figure 2 shows a SEM image (panel a) and a reflectivity curve (panel b) of a TiO_2 thin film deposited by means of PMCS on a Pt coated substrate, similar to the one used for the aluminum oxide. The reflectivity curve is measured in normal incidence and is fitted by a model taking into account the reflection by the Pt substrate and the porosity of the TiO_2 film. A χ^2 minimization routine gives a thickness of the film of 35 nm and a porosity of 23 %. Further details on the analysis will be given elsewhere.

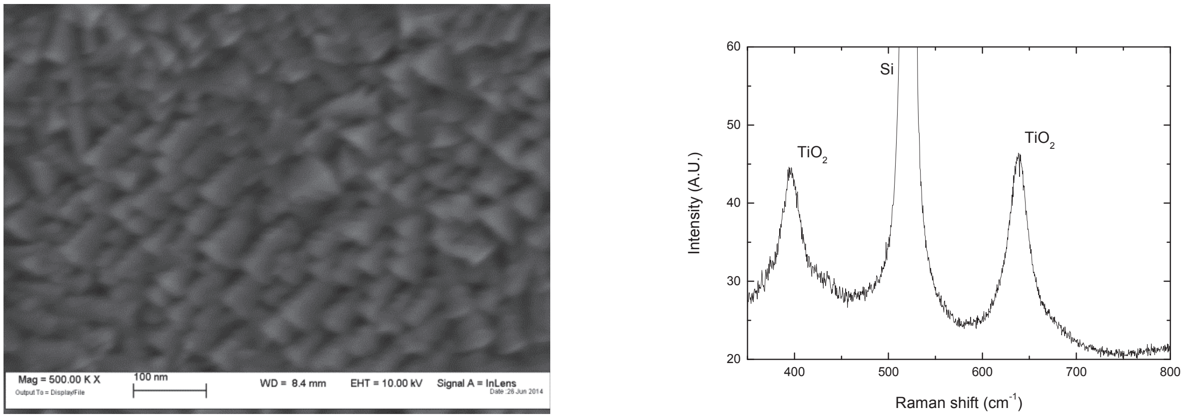


(a)

(b)

FIGURE 2. Morphological and optical characterization of a thin film of TiO_2 grown by PMCS. Panel a): SEM image of the oxide film at a magnification of 469Kx. Panel b): reflectivity curve in normal incidence of the TiO_2 film on a Pt substrate. The error bars (green) indicate ±σ uncertainties. The line (red) is the best fitting curve.

For the ALD deposition of TiO_2 we used water and titanium isopropoxide as reagent, with He as carrier gas. The film is deposited on a Si substrate for the SEM and Raman characterizations and on a Pt coated substrate for the electrical measurements. The TiO_2 thin film is grown at 300 °C and 20 mbar, with 100 ALD cycles for a nominal thickness of 40 nm. Raman spectra made on samples thicker than the ones actually used for the memristor suggest that the films have anatase crystal structure, with distinctive peaks at 395 cm^{-1} and 640 cm^{-1}, as shown in Fig.3b. The SEM images also confirm the presence of nanocrystallites (Fig. 3a).



(a)

(b)

FIGURE 3. Morphological and structural characterization of a thin film of TiO_2 grown by ALD on a Si substrate. Panel a): SEM image of the oxide film at a magnification of 500Kx. Panel b): Raman scattering of the film obtained with a 50x magnification lens and a 50 mW laser source at a wavelength of 473 nm with a T64000 spectrometer operated in single pass configuration.

Current-voltage curves have been measured on devices made both with PMCS and ALD deposited TiO_2 films. As a top electrode we used a thin Pt wire and the Pt/TiO_2/Pt stack showed the expected pinched hysteresis loop, after a few forming cycles.

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