



Highly conductive titanium oxide nanotubes chemical sensors



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ABSTRACT

Nb–TiO₂ nanotubes arrays have been prepared by anodisation of Nb–Ti metallic films. After the annealing treatment the nanotubes are crystallized in the anatase phase. Conductance increased of several orders of magnitude thanks to the introduction of Nb. We have prepared conductometric sensors and evaluated their sensing properties towards different gases. Functional measurements demonstrated very good sensing performances towards ethanol, acetone and carbon monoxide. The gas sensing performances has been tested as a function of the dimensions of the nanotubes showing an improvement in chemical sensing as the internal diameter of the tubes get smaller.

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1. Introduction

Downscaling materials to the nanometer size draws the attention of researchers thanks to the interesting, peculiar and sometimes even surprising properties that nanosized configuration shows compared to their bulk counterparts. Titania, together with zinc oxide, is one of the most studied semiconducting oxides for functional applications. Numerous studies focus on nanostructured titania properties for different fields of application like chemical sensing, solar cells, photocatalysis, Li-ion battery [1–7].

Titania thin films may be prepared with different techniques ranging from liquid to vapor phase procedures. Furthermore the advantages of metal oxides in form of nanoparticles, i.e. large surface-to-volume ratio and a Debye length comparable to their dimensions, increase the use of titania in above mentioned emerging applications [8,9]. A key aspect is the ability to finely tune its morphology and grains dimension for a reliable integration into devices.

Very few methods have been developed for fabrication of highly ordered TiO₂ nanostructures [10–12]. In contrast to other methods, electrochemical anodization tailors the morphological features of the structures (pore diameter, interpore distance, wall thickness and length of the tubes). Furthermore, the preparation may be

carried out at room temperature. Vertically aligned nanotubes grow on the substrate starting from a metallic titanium film or foil, without other precursors or assisting layers [13,14] to enhance the growth. TiO₂ nanotubes obtained by electrochemical anodization are amorphous, crystallization may be achieved through post-growth thermal annealing which is the main drawback of this fabrication method [15].

Titanium oxide is one of the most promising candidate materials for fabrication of sensing devices such as chemical sensors. Nanostructures modifications with controlled morphological, structural and electrical properties and higher surface areas are key features for the preparation of effective chemical sensors. Yamazoe and Shimano reported an increase in gas sensing performances as the grain size decreases and better sensing properties of nanotubular oxide structures compared to traditional thin film [16,17].

There are several bottlenecks limiting the performances of the state of art devices, first of all TiO₂'s high resistivity [18], that requires expensive equipment for the signal read out, and furthermore the agglomeration of nanoparticles with high temperature long term operation, that reduces the sensors reliability [19].

Bandgap engineering through doping may improve material electrical transport properties [20–22]. Doping with elements like Nb is a way to tune electrical properties, as confirmed by both theoretical and experimental studies. There are several studies on thick or thin films Nb doped titania for chemical sensing [23–31]. While still only a few references can be found on the chemical sensing of Nb doped titania nanotubes structures, we have already

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prepared (Ref. [21]) Nb-doped (0.14 at%) titania nanotubes by anodisation of a Nb–Ti thin film. Such a low concentration achieved by placing Nb insets in a Ti target was enough to remarkably improve the sensing performances and the conductance, indeed the latter was still not compatible with standard electronics. Therefore we present here the performance of heavily Nb doped titania nanotubes achieving acceptable conductivity values.

2. Experimental

We prepared titania nanotubes films by electrochemical anodization.

2.1. Deposition and electrochemical anodization of Nb–Ti films

We deposited Nb–Ti thin films on alumina substrates by means of RF (13.56 MHz) magnetron sputtering, employing a (4" in diameter) titanium–niobium alloy 5 wt% (certified at 99.9% purity) target (4" in diameter). During the deposition, Ar pressure in the sputtering chamber was 5×10^{-3} mTorr, sputtering power was 75 W and the alumina substrates were heated at 300 °C. The distance between the target and the sample was 7 cm, and the deposition time 70 min. The thickness of the metallic films was 500 nm.

The formation of Nb–TiO₂ nanotubes was obtained by electrochemical anodization of Nb–Ti layer by potentiostatic mode using a two-electrode configuration. A Pt foil act as the counter electrode and 0.8 wt% NH₄F and 0.5–2 mol L⁻¹ H₂O contained glycerol the electrolyte. The applied voltage between the electrodes ranged between 20 and 60 V and the anodization time was 30 min. After anodization the samples were washed in distilled water and dried at room temperature. Thermal annealing in a 50% O₂ and 50% Ar atmosphere at 400 °C for 6 h induced the crystallization of the as-prepared samples.

2.2. Fabrication of functional devices

Metal layers were deposited on 2 mm square alumina substrates for the preparation of functional devices. After the anodisation process, platinum electrodes with interdigital geometry and the heater were deposited by means of RF magnetron sputtering on the front and backside of the substrate without affecting the surface morphology.

2.3. Morphological and structural characterization of the samples

The morphology and composition of the samples was investigated by means of scanning electron microscopy (SEM) using a LEO 1525 microscope equipped with field emission gun and Energy-dispersive X-ray spectroscopy.

Grazing Incidence X-Ray Diffraction (GIXRD) experiments were performed by means of a Bruker 'D8 Advance' diffractometer equipped with a Göbel mirror and a CuK α radiation tube ($\lambda = 0.154$ nm). The incidence angle was fixed at 0.5°, to be more sensitive to films structure [32].

2.4. Electrical and functional characterization

The electrical properties have been tested at constant temperature, atmospheric pressure and 40% RH@20 °C in air. In order to test the functional properties of the nanostructures we investigated a wide range of operating temperatures and different gases such as carbon monoxide, nitrogen dioxide, ethanol, acetone and methane. Gas tests were performed with the flow-through technique in a thermostatic sealed chamber at 20 °C, 40% relative humidity and at

atmospheric pressure, using dry air as a carrier gas (flow rate = 0.3 slm). A detailed description of the experimental setup and the contact geometry is reported elsewhere [33]. The layers were kept at each operating temperature for 10 h before gas injection, the sensor resistance was measured as a function of the gas concentration using the volt-amperometric technique at 1 V constant bias. The sensor responses were calculated as the relative resistance/conductance variation upon exposure to the target gases for oxidizing/reducing reactions, respectively. Response time was calculated as the time necessary for resistance/conductance to reach 90% of steady state, whereas recovery time the one needed to recover to 30% of the resistance/conductance when back to air.

3. Results and discussions

3.1. Structural, compositional and morphological analysis

Glancing Incidence X-Ray Diffraction (GIXRD) measurement of the sample was reported in Fig. 1. The pattern shows some intense XRD peaks that can be attributed to anatase phase.

It was already shown [34,35] that Nb as a dopant of TiO₂ powder produces the change in the anatase microstructure, inducing microstrains, but no segregation of Nb oxide phases was found even with thermal treatment at 500 °C. The reported results are in agreement with our GIXRD data, where only anatase phase is detected.

EDX analyses of the layers before and after the anodization process confirmed the homogeneous presence of 4.5 ± 0.5 wt% of Nb with respect to Ti which was consistent with the concentration of the target.

Electrochemical anodization is based on two continuous processes, one is oxidation of metal at the oxide/metal interface ($\text{Ti}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+$) and the other is oxide dissolution at the electrolyte/oxide interface ($\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O}$) [36,37]. The morphology of the anodized TiO₂, besides the anodization voltage and the time, is also strongly depending on ratio of glycerol versus water [38]. In Ref. [38] self-assembled TiO₂ nanotube arrays with controllable diameter and length have been successfully obtained and the presence of an optimal volumetric ratio between water and glycerol was reported.

Concerning anodisation of Ti–Nb nanotubes, as long as the samples were anodized in 2 M contained electrolyte the nanostructures were porous (Fig. 2(a)). Probably titanium oxidation rate

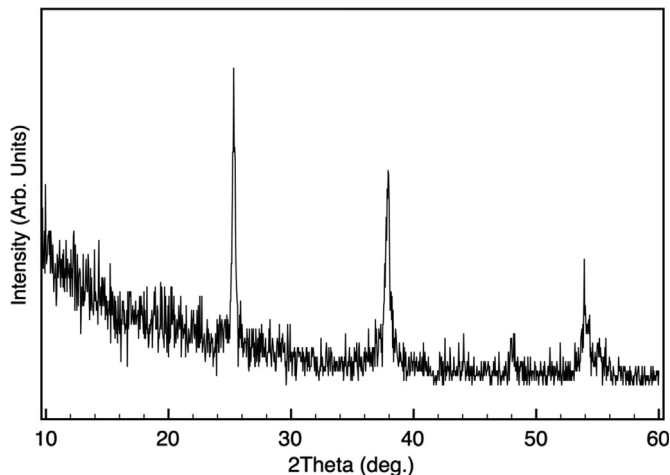


Fig. 1. GIXRD measurement performed at 0.5° of incidence. All the peaks in the X-Ray diffraction pattern can be attributed to the anatase phase (JCPDS files no 021-1272).

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