

# Semiconducting properties of self-organized TiO<sub>2</sub> nanotubes

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## Abstract

The semiconducting properties of anodic grown TiO<sub>2</sub>-nanotubes were analyzed by means of the potential dependence of the interfacial capacity under different electrolyte and illumination conditions. The experimental results offer evidence for a duplex oxide film conformed by the bottom and wall of pores with different density of donors and concentration of surface states. The surface extension offered by the walls of oxide tubes is manifested in surface related effects such as the shift of the flat band potential and trapping of photoelectrons.

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## 1. Introduction

The semiconducting and photoelectrochemical properties of TiO<sub>2</sub> [1] makes this material very interesting, essentially for its applications in the construction of photo-catalysts and solar cells. This motivated a series of studies about the anodic formation of uniform and compact layers of TiO<sub>2</sub> in different electrolytes [2–4]. However, a renewed interest in this material was shown in the last years, especially in the production of porous TiO<sub>2</sub> as a mean to enhance its surface properties. Various methods were developed to generate nano-porous titanium oxides with a high specific area, mostly based on the sintering of nano-particles obtained by sol–gel procedures. Further modifications and improvements of these surfaces were performed by annealing [5–7], doping with nitrogen [8] or carbon [9] or by attaching suitable organic dyes, as commonly made for the optimization of solar cells [1,10,11]. Recently, the formation of highly organized porous layers of TiO<sub>2</sub> by anodization in fluoride containing electrolytes was investigated and optimized with a great success [12–17]. This fact allowed extending the feasibility of this material for technological applications not only due to the highly organized structure but also due to the good electrical contact with the substrate, which presents some advantages in an attempt to introduce more simple assemblies in the construction of photo-chromic devices.

The aim of this paper is to advance in the understanding of the semiconductor properties of tubular TiO<sub>2</sub>, necessary to find optimal conditions in the numerous applications involving chemical, electrochemical and photoelectrochemical processes at the semiconductor/electrolyte interface.

## 2. Experimental details

The anodization and electrochemical characterization were performed in a classical cell with a three electrode arrangement with non deaerated solutions. A Pt sheet and a Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub>(sat) system were used as a counter and reference electrode, respectively. Oxide layers were formed anodically following the same preparation procedure from Ti sheets (99.6% purity) and using the same equipment as reported in Ref. [12]. In this way the following layers were produced:

- (i) Compact layers: 1 M H<sub>3</sub>PO<sub>4</sub> ( $U_{ox} = 10$  V,  $\tau = 10$  min, oxide thickness ca. 25 nm).
- (ii) Short tubes: 1 M H<sub>3</sub>PO<sub>4</sub> + 0.3% HF ( $U_{ox} = 10$  V,  $\tau = 2$  h, thickness  $\sim 500$  nm).
- (iii) Long tubes: 1 M NaH<sub>2</sub>PO<sub>4</sub> + 0.5% HF ( $U_{ox} = 20$  V,  $\tau = 2$  h, thickness  $\sim 1$   $\mu$ m).

A subsequent thermal annealing of the oxide layers was carried out at 450 °C in air during 3 h using a heating and cooling rate of 20 °C/s in order to convert the amorphous oxide in anatase [17,18]. Fig. 1 shows the morphologies of the porous structures

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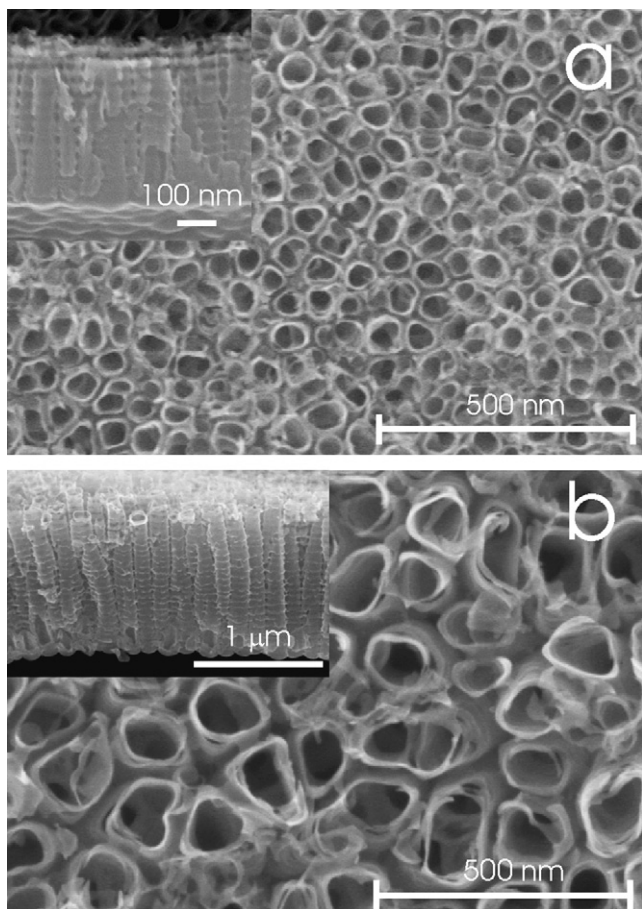


Fig. 1. SEM top view and cross sections for the porous layers formed after anodization in: (a) 1 M  $\text{H}_3\text{PO}_4$  + 0.3% HF at 10 V and (b) 1 M  $\text{H}_2\text{NaPO}_4$  + 0.5% HF at 20 V.

with different pore geometries, namely short pores of 75 nm of diameter (method ii) and long pores with an aperture of 150 nm (method iii). The thickness of the pore walls is difficult to be determined by SEM but it can be estimated to be between 20 and 30 nm.

Acetate and borate buffer solutions of pH 2.73–9 were used for the capacitance analysis. Except for photoelectrochemical measurements, all runs were performed in the dark.

The surface morphology of nano-structured layers was characterized by means of a scanning electron microscope Hitachi SEM FE 4800. Impedance measurements were carried out with a universal electrochemical interface and an impedance spectrum analyzer Zahner IM6d. Experiments under illumination were performed using a 150 W Xe lamp coupled to an Oriel 7400 1/8 monochromator and an electrochemical cell with a flat quartz window.

### 3. Results and discussion

#### 3.1. Polarization curves

Polarization experiments generally offer a first approach for understanding the electrochemical behavior of the interface oxide/electrolyte. Fig. 2 shows that the cathodic polarization

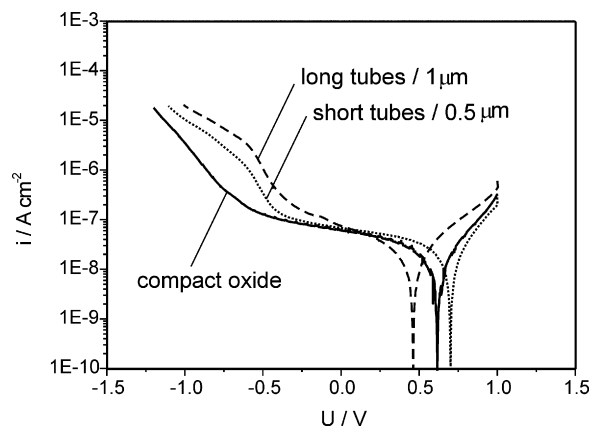


Fig. 2. Polarization curves performed in acetate buffer solution of pH 6 on compact and porous oxides.  $U_{sa} = 1$  V,  $U_{sc} = -1.0$  V,  $v = 5$  mV s $^{-1}$ .

curves performed on compact and porous oxides are characterized in all cases by a current plateau followed by an exponential increase at  $U < -0.5$  V. The fact that this behavior was also observed after deaerating the solution with nitrogen, leads to ascribe it exclusively to different charge transfer mechanisms for the hydrogen evolution. As it will be discussed later, this change may be ascribed to the disappearance of the Schottky-barrier control on approaching the accumulation zone of the semiconducting oxide and the onset of a kinetic-controlled electron transfer. On the other hand, the presence of an anodic current at potentials between 0.5 and 1 V points out the start of oxygen evolution promoted by injection of holes from the valence band.

A marked difference between the current densities of the compact and porous oxides can be observed at  $U < -0.5$  V, which is mainly related to the larger active area of the oxide tubes. However, practically no differences can be discerned at  $U > -0.5$  V, indicating a common controlling step in the charge transfer mechanism. These features are probably a consequence of a two-film structure conformed by a compact base oxide and a porous overlayer.

To throw more light on the electronic transfer of the different oxides, polarization curves were performed in a solution containing the couple  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  (Fig. 3). It must be noted that in this case the polarization curves reflect the main characteristics of the electron transfer in semiconductors, that is, a Schottky barrier and a kinetic control in the depletion and accumulation zones of the  $n$ -semiconductor, respectively. Here, the presence of an extended surface area in the porous layers is pointed out by a shift of the anodic polarizations toward higher current values. On the other hand, the cathodic polarizations practically do not show any difference between the two porous oxides, similarly as it was observed in the case of hydrogen evolution.

Relations  $i_{\text{porous}}/i_{\text{compact}}$  of 9 and 194 for the 0.5 and 1  $\mu\text{m}$  long tubes, respectively, were obtained by comparing the anodic polarizations. This result makes it difficult to relate directly the increase of the anodic current with the increase of surface area. Here, the electronic structure of the semiconductor seems to play a key role.

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