Anodisation of sputtered titanium films: an electrochemical and electrochemical quartz crystal microbalance study

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Abstract

Smooth titanium films were deposited by cathodic sputtering on glass substrates in order to avoid the more sophisticated polishing procedure of bulk titanium. The titanium films were then anodised in a sulphuric acid solution, using two different procedures: galvanostatic (1.5 mA/cm^2) and potentiostatic (10 V vs. Ag–AgCl) conditions. Atomic force microscopy (AFM) shows that the potentiostatic TiO$_2$ is rougher than the galvanostatic one. Mott-Schottky experiments confirm the n-type semiconductor behaviour of both TiO$_2$ films. However, differences between their flat-band potentials and their donor concentration values are apparently due to this difference of roughness. Finally, electrochemical quartz crystal microbalance (EQCM) measurements were carried out and appeared necessary to study the kinetics of the TiO$_2$ growth.

1. Introduction

Titanium is a valve metal well known to have good corrosion resistance attributed to a passive titanium oxide film at the metal surface. This oxide layer shows semiconductor behaviour, with a band gap of 3.1 eV. Titanium oxide passive films find applications in many fields: surface protection, biomedical or aerospace engineering and photocatalytic engineering [1]. Their optical properties are used for antireflection films. The n-type semiconductor properties allow the reduction of various redox systems such as copper [2], when the titanium oxide film is polarized cathodically. It is also of fundamental importance for electrochemical and chemical industries. Ti/TiO$_2$ are substrates of dimensionally stable anodes, which are used for chlorine production [3]. Furthermore, fundamental aspects of nucleation can be

studied (reduction of noble cations such as platinum [4]). Much literature is devoted to titanium oxides produced by various techniques such as sol–gel [5], chemical vapour deposition (CVD) [6], physical vapour deposition (PVD) and electrochemical anodisation of bulk titanium (galvanostatic, potentiostatic or potentiodynamic pathways [7,8]). The stability and electrochemical properties of the TiO$_2$ layer depend on its preparation mode but also on the mode of preparation of the titanium substrate itself. In order to perfectly control the elaboration of the Ti/TiO$_2$ interface, a sophisticated procedure of mechanical and electrochemical polishing has to be carried out [4]. Our approach has been to short-circuit this stage by directly producing titanium films by sputtering on smooth substrates (glass) [9]. They were anodised using potentiostatic and galvanostatic polarizations. The different morphologies between the two films have been highlighted by atomic force microscopy (AFM) measurements. The semiconductor properties of the titanium oxide films were characterized by electrochemical impedance spectroscopy measurements (Mott-Schottky measure-

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ments). Finally, we have studied the formation and evolution of the film thickness using an electrochemical quartz crystal microbalance (EQCM) during the titanium anodisation.

2. Experimental details

2.1. Physical vapour deposition

Titanium films were sputtered with a direct current triode system on glass and quartz substrates, which were previously cleaned using an ultrasonic rinse in ethanol.

The titanium target was disk-shaped with a diameter of 5 cm. The base pressure prior to deposition was typically in the 10^{-7} Torr range. The titanium deposit was prepared on glass substrates for 20 min, leading to a thickness of about 500 nm, and on titanium covered 5 MHz quartz crystals (Maxtek) for 40 min, leading to a thickness of around 1000 nm.

2.2. Atomic force microscopy (AFM)

The average surface roughness of the samples before and after anodisation was measured with an Autoprobe CP (Park Scientific Instrument) used in contact mode. All AFM measurements were performed in air at 25 °C with a silicon nitride cantilever.

2.3. Anodisation of titanium substrates

The electrochemical cell containing a 0.5 M sulphuric acid solution at room temperature, and a traditional three-electrode assembly was used with platinum as the counter electrode and Ag/Ag–Cl as the reference (E=0.197 V vs. NHE). Titanium films on glass substrates were embedded in a polymeric resin to expose only a test area of approximately 1 cm^2.

Before anodisation, the titanium electrode was conditioned at open-circuit potential in a H_2SO_4 solution for an hour, to reach a stationary value (E_{corr}). Two procedures were retained for the oxide growth: a potentiostatic anodisation at 10 V vs. Ag–AgCl during 1 or 2 h and a galvanostatic anodisation at 1.5 mA/cm^2 during the same time.

2.4. Electrochemical characterization

2.4.1. Electron transfer reaction

Potentiodynamic measurements were performed in a 0.1 M $K_3Fe(CN)_6$/$K_4Fe(CN)_6$ solution with a scan rate of 2 mV/s starting from the cathodic potentials towards the anodic potentials in visible light.

2.4.2. Mott-Schottky measurements

Mott-Schottky measurements were carried out in a 0.5 M sulphuric acid solution with a 10 mV amplitude signal, a frequency range from 10^6 Hz to 100 mHz, starting from the anodic potentials (2 V vs. Ag–AgCl) towards the cathodic potentials (−0.5 V vs. Ag–AgCl), with an increment of 100 mV. All electrochemical measurements were performed with a frequency response analyser (Solartron 1260) connected to a potentiostat (Solartron 1287). Impedance diagrams were interpreted on the basis of equivalent circuits using Zview (Solartron Software).

2.4.3. Electrochemical quartz crystal microbalance experiments

EQCM experiments were performed using a commercial model PM-170 Planting Monitor (Maxtek) in a 0.5 M H_2SO_4 solution.

The quartz used (Maxtek) has a fundamental frequency of 5 MHz and is in the form of thin disks of 2.5 cm in diameter. The quartz crystals were placed on a vertical PTFE sample holder. The variation of the quartz vibration frequency Δf is directly related to a mass variation Δm on the quartz surface and follows the Sauerbrey equation: $\Delta f = -C_m \cdot \Delta m$ where $C_m = -\frac{2f_0^2}{\sqrt{\mu_q \rho_q}}$, f_0 is the fundamental resonance frequency (5 MHz) of quartz, μ_q its shear modulus ($2947 \cdot 10^{11}$ g cm^{-1} s^{-2}) and ρ_q its density (2648 g cm^{-3}). The EQCM was connected to the working electrode output of the potentiostat. Mass change and potential/current measurements were thus simultaneously performed.

3. Results and discussion

3.1. Atomic force microscopy micrographs

Fig. 1a shows an AFM image performed on a titanium film deposited on glass substrates. The roughness measurements point out that the film is very smooth with a mean roughness of only 1 nm. This confirms the interest of titanium films deposed by PVD with respect to more sophisticated polishing methods. Titanium oxide films were grown using potentiostatic and galvanostatic procedures in a sulphuric acid solution. The two samples were characterized by AFM and electrochemical experiments, which showed differences between the two oxides formed. On Fig. 1b and c are presented the AFM images made on the oxide grown under galvanostatic conditions (Fig. 1b) and under potentiostatic conditions (Fig. 1c). The roughness of the potentiostatic TiO_2 film (11 nm) is about twice higher than that of the galvanostatic film (4.5 nm). Those roughness values are higher for the oxides than for the initial metal film. Finally, one can observe that the grain size is smaller and the film structure is more compact for the galvanostatic TiO_2 than for the potentiostatic oxide.

Globally, all these roughness values remain relatively weak and it should be stressed that these values could be reduced by using a smoother substrate.