



Impedance behaviour of anodic TiO₂ films prepared by galvanostatic anodisation and powerful pulsed discharge in electrolyte

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ARTICLE INFO

Article history:

Received 5 February 2012

Received in revised form 15 May 2012

Accepted 19 May 2012

Available online 29 May 2012

Keywords:

Anodic films

Titanium dioxide

Pulsed discharge

EIS

Photocurrent

ABSTRACT

Anodic titania films were prepared on titanium by novel powerful pulsed discharge technique which confers extremely high rates of the film growth. Electrochemical impedance spectroscopy (EIS) has been used as a main method to study the structure and semiconductive properties of the anodic oxide films grown in sulphuric acid electrolyte. The EIS results are supported with microscopic observations and photoelectrochemical measurements. For comparison, the properties of the anodic films prepared by the conventional galvanostatic anodisation in the same electrolyte were also examined. For modeling of the impedance spectra, different equivalent circuits taking into account the effects of space charge region and film structure were proposed. Thinner anodic films ($d \approx 25$ nm) prepared by both methods demonstrate a similar behaviour characteristic of amorphous barrier-type oxide, whereas a very significant difference in the properties of the films produced by the two different approaches was revealed for thicker films ($d = 70$ – 120 nm). The discharge-prepared films in this range of thickness are composed by one compact layer with a relatively low concentration of ionised donors ($N_d = (1-3) \times 10^{18} \text{ cm}^{-3}$) estimated from Mott–Schottky plots, whilst the conventional galvanostatic method leads to the development of two-layer films consisting of an inner compact layer and a nanoporous outer one. The latter samples exhibit a significantly reduced photocurrent response at short wavelengths and an essentially higher concentration of ionised donors as compared with the films obtained by the pulsed discharge method.

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1. Introduction

Titanium and its alloys are widely used in different applications owing to their good mechanical properties and a high corrosion resistance in various media [1–3]. The latter is provided by a chemically stable oxide film which spontaneously forms on titanium. Electrochemical oxidation (anodisation) of titanium and its alloys provides thicker oxide layers demonstrating improved protective and functional properties [4,5]. Thin films of titania have very high potential to be used for fabrication of memristors [6]. The memristance arises naturally in nanoscale systems in which solid-state electronic and ionic transport are coupled under an external bias voltage [7]. The thickness and defect structure of the titania films has a significant effect on the memristance properties [6].

It has been shown that the properties of the anodic films on titanium depend greatly on the conditions at which the film is grown [8–16]. One of the important factors affecting the characteristics of

the anodic films is their growth rate. Blackwood and Peter reported that the relative dielectric constant, ϵ , and defect concentration profiles in the oxide film depend markedly on the film growth rate [11]. Ohtsuka and Otsuki revealed that the ϵ value increases and the ionised donor concentration decreases with increasing the growth rate of the anodic film on titanium [14]. The refractive index of the anodic TiO₂ films was also found to be smaller with the higher growth rate [13].

Recently we have demonstrated the application of the high-voltage pulsed discharge technique for creation of thin anodic films on titanium [17]. Under the action of single powerful electric discharges in electrolyte, extremely high rates (400–700 $\mu\text{m/s}$) of the oxide film growth were reached on the titanium anode. The growth rate is the fastest ever reported. The results of Auger depth profiling showed that the oxide films prepared by the pulsed discharge method are characterised by higher stoichiometry and more homogeneous distribution of basic elements (Ti and O) through the film thickness in comparison to the films grown by the conventional galvanostatic anodisation [17]. Moreover, enhanced photoelectrochemical activity was revealed for the pulse discharge-prepared films motivating their further investigation. Also preparation of oxide films on pure aluminium electrodes using the powerful

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pulsed discharge technique was studied [18]. It was found that dense one-layer alumina films with thicknesses up to 200 nm can be created on the Al surface. Scanning Kelvin Probe Force Microscopy (SKPFM) measurements showed that the anodic alumina films prepared by the pulsed discharge method have more uniform surface structure and electrical properties which are less dependent on the initial surface conditions than those of the films prepared by the conventional anodisation methods.

Electrochemical impedance spectroscopy (EIS) is a powerful technique for in situ characterisation of various oxide films on metal surfaces. This technique was successfully applied to examine anodic oxide films on different valve metals such as Al [19–21], Zr [22], Nb [23]. EIS was also used to characterise oxide films on titanium surface [24–40]. Blackwood [24] investigated the impedance response from very thin (several nanometers) passive oxide films on titanium and showed that the contribution of the space charge region (SCR) formed in the oxide layer must be taken into account when interpreting the impedance data. In a number of EIS studies [29,30,34], impedance spectra of thin anodic films on titanium exhibit a single time constant, which is indicative of a uniform compact layer, whereas thicker films tend to reveal a second time constant in the impedance spectra. In the latter case, the interpretation of the EIS data was based on a two-layer model of the oxide film composed by a thin intact inner layer and a porous outer layer [25,29–31,34,39,40].

In the present work, electrochemical impedance spectroscopy has been used as the main method for characterisation of the structural features and semiconductive properties of novel anodic oxide films formed on titanium at extremely high growth rates under the powerful pulsed discharges (hereafter referred to as PD films). For comparison reasons, impedance spectra recorded on the films grown by the conventional galvanostatic oxidation (hereafter referred to as GS films) are also discussed. The photoelectrochemical method as well as transmission electron microscopy (TEM) accompanied with electron diffraction were also applied for studying the anodic oxide films to support the selection of the equivalent circuits and the conclusions drawn from the EIS measurements.

2. Experimental

Titanium plates (8 mm × 70 mm; 99.8% Ti) used as working electrodes were polished mechanically and then chemically in HF:HNO₃ (1:3 by volume) mixture to mirror finish and finally rinsed with deionised water. Part of the surface was isolated with epoxy resin, giving an electrode working area of 6 cm². The electrochemical cell used for the pulsed discharge oxidation of Ti was constructed from high-impact polystyrene and consisted of a titanium anode placed in the centre of a cylindrical Ti cathode with 20 times larger surface area. 1 M H₂SO₄ aqueous solution ($T = 25 \pm 1$ °C) was used as an electrolyte. Electric discharges in the electrode system were generated using a low-inductive 100 μF capacitor bank charged to a definite voltage (1350 V) which was commutated with a low-inertial relay triggered by a synchronizing pulse. Duration of discharge was less than 20 μs. Conventional galvanostatic anodisation of the titanium electrodes was performed in the same cell at a current density of 10 mA cm⁻² using a controllable dc power supply.

The EIS measurements were performed using a Gamry FAS2 Femtostat with a PCI4 Controller in a 10⁵ down to 10⁻² Hz frequency range with a step of 10 points per decade. Impedance spectra were recorded applying a 10 mV sinusoidal perturbation at open circuit potential or at different potentials in the range from 0.8 V to -0.4 V vs. SCE. The EIS measurements were carried out at room temperature in a conventional three-electrode cell consisting of a saturated calomel reference electrode (SCE), a platinum

foil as the counter electrode and the working electrode with an exposed area of 1 cm². The cell was placed in a Faraday cage to avoid interferences with external electromagnetic fields. The working solution was 0.1 M acetate buffer (pH 6). To remove oxygen, the solution was purged with argon. Before the spectra recording, the system was allowed to attain a stable open circuit potential or a quasi-stationary current under potentiostatic polarisation. At least two samples prepared under the same conditions were tested to ensure reproducibility of the results. The impedance plots were fitted using different equivalent circuits by means of the Elchem Analyst software from Gamry Inc.

Photocurrent spectra were recorded in a quartz cell having an optical quality window. A setup equipped with a high-intensity grating monochromator, a 1000 W xenon lamp and a slowly rotating light chopper (0.3 Hz) was used for monochromatic irradiation of the working electrode. Photocurrent spectra were corrected for the spectral intensity distribution at the monochromator output measured by a calibrated thermocouple power meter.

TEM measurements were performed on a Hitachi H9000 transmission electron microscope at an acceleration voltage of 300 kV. Electron transparent sections for TEM with a thickness of 15 nm were cut using a Leica Reichert Supernova ultramicrotome. To prepare the samples, titanium electrodes with an oxide film were embedded into resin and polished from the metal side up to a thickness of 10–15 μm, and then they were re-embedded into resin. A cut with a width of 10 μm was then made using an ultramicrotome with a glass knife. Obtained microrod (10–15 μm × 10 μm × 3–4 mm, oxide is on the one of faces) was embedded once more into resin, perpendicular to the cut, and finally was sliced with a diamond knife (Diatome 45°).

3. Results and discussion

3.1. Anodic oxide film formation

Upon the action of powerful electric discharge on the electrode system, the extremely rapid growth of the oxide film on titanium anode surface is observed. An electric charge of 0.0225 C cm⁻² was passed through the Ti electrode–electrolyte interface during one discharge, resulting in the formation of 25 nm thick anodic film as shown in our previous work [17]. The subsequent discharges lead to step-wise increase in the film thickness visually observed as a characteristic change of the interference colour. The colour properties of anodic oxide films on titanium have been previously shown to originate from light interference [41]. The average thickness of the obtained anodic films was estimated by the depth profile analysis using Auger electron spectroscopy as described in detail in our previous work [17]. For relatively thick films (120–170 nm) the thickness values were also confirmed by TEM observations (Fig. 1). The films obtained by the discharge approach appear to be intact and uniform.

For comparison, the anodic films on titanium were also prepared by the conventional galvanostatic anodisation in the same electrolyte at a current density (j) of 10 mA cm⁻². The duration of the galvanostatic anodisation was chosen so that the thickness of the GS films was coincident with that of the PD films. This makes possible more correct comparison of the properties of the anodic films prepared by these two methods. The anodizing ratio (the ratio between the oxide film thickness, d , and the maximum film formation voltage, U_{\max}) calculated for the galvanostatic growth of anodic TiO₂ films was about 2.78 nm/V and slightly decreased down to 2.65 nm/V for the films with $d > 120$ nm. This estimate is in a good agreement with the anodizing ratio values (2.5–3 nm/V) more commonly reported in literature for the titania anodic films grown in sulphuric acid solutions [8,10,37,41–43].

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