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Anodic titanium oxide photonic crystals prepared by novel cyclic anodizing with voltage versus charge modulation



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<i>Keywords:</i> Anodic titania Anodizing Photonic crystals Porous structure Film	Photonic crystals based on titania are of great practical importance in modern photonics owing to a variety of possibilities for their applications in optoelectronics, sensorics, and solar photovoltaics. However, the reproducible, scalable, and low-cost method of the preparation of titania photonic crystals with desired optical characteristics is still absent. Here the novel anodizing regime with voltage versus electric charge modulation, <i>U</i> (<i>Q</i>), is suggested for the precise morphology control of anodic porous films of valve metals oxides. The potential of the suggested approach is demonstrated on the preparation of high-quality one-dimensional titania photonic crystals. A new type of anodic itiania nanotubes possessing periodic change of inner diameter and constant outer diameter is prepared using sine-wave modulation of applied voltage with electric charge. The possibility to tune

the position of photonic band gap within the whole visible spectrum is shown.

1. Introduction

Photonic crystals made of titania attract great attention owing to perspectives for practical applications in optoelectronics, sensorics, and solar photovoltaics. They are caused by the synergy of anomalous dispersion in photonic crystals and of unique properties of titania, such as a high refractive index ($n_{\text{TiO}_2} = 2.6 \text{ at } \lambda = 600 \text{ nm [1]}$), high chemical stability, low toxicity, semiconductor conductivity, and electrochromism.

One of the promising methods of the preparation of titania with controlled nanomorphology is titanium anodizing in pore-forming electrolytes [2–4]. In the case of valve metal anodizing under periodically changing conditions one can obtain porous oxide film with periodic modulation of porosity across the thickness [5–8]. This kind of anodic oxide films can be considered as one-dimensional photonic crystals because the effective refractive index changes periodically along the surface normal.

The first results on anodizing of titanium at periodically alternating voltage were reported in 2008 [9]. It has been shown that obtained under square-wave voltage modulation anodic titanium oxide (ATO) films, consisted of bamboo-like titania nanotubes, show higher efficiency of solar energy conversion in dye-sensibilized solar cells in comparison with titania nanotubes with smooth walls [10]. It is worth noting that in the case of periodic variation of voltage with time, the accurate periodicity of porosity modulation in ATO cannot be achieved.

The layer thickness formed during one cycle of anodic oxidation decreases gradually from cycle to cycle due to the decrease in current with the increase in porous film thickness [11].

In 2011, ATO photonic crystals with well-defined photonic band gaps were obtained under periodically alternating current conditions [12]. The resulting structure of porous titania contained tubes with periodically tapering and expanding of outer diameter and was therefore called "concave". Later, the alternating-current anodizing of titanium has been successfully applied for the preparation of anodic titania films with extended periodical morphology used as one of the components of dye-sensitized solar cells [11,13–17]. Several complex time-dependencies of periodic voltage pulses have been proposed for the preparation of porous multilayer films [18,19] and structures similar to the "concave" type ATO [20].

The positions of the photonic band gaps depend on the composition of the medium inside the pores of ATO, that makes possible to use ATO photonic crystals as refractive index sensors [20,21]. Moreover, the optical response of anodic titania photonic crystals can be reproducibly switched on/off by an anodic/cathodic polarization [18]. This effect can be used to create smart color windows or electronic displays.

To the best of our knowledge, all anodizing regimes, which have been previously applied to prepare one-dimensional ATO photonic crystals, used either time-periodic voltage or current profiles. However, as was previously noted, titanium anodizing with periodic U(t) profile leads to different layer thickness in the upper and the lower parts of the

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film. On the other hand, in the case of periodic I(t) profile, anodizing voltage increases from cycle-to-cycle that also break the optical periodicity.

Here, we propose a new anodizing regime with voltage versus electric charge modulation U(Q). In situ measuring of charge allows us to control the thickness of the layers with high precision, whereas control of voltage guarantees the identity of voltage-dependent parameters of the ATO structure for each layer from the top to the bottom. The ability to design the morphology of anodic oxide films using the suggested approach has been demonstrated on the example of the synthesis of one-dimensional photonic crystals.

2. Materials and methods

Before anodizing, the titanium foils (99.6% purity, 0.15 mm thick) were electrochemically polished in the mixture of 99.5 wt% acetic acid and 65 wt% perchloric acid with a volume ratio of 9:1. Electropolishing was conducted at temperature below 25 °C during 4 min under square-wave applied voltage: 40 V for 10 s and 60 V for 10 s. Ti was anodized in an ethylene glycol (EG) electrolyte containing 0.3 wt% NH₄F, 0.66 wt% CH₃COONa (NaAc), and 2 wt% H₂O at 30 °C using programmable DC power supply. The electrolyte was agitated at the rate of 480 RPM using overhead stirrer. The distance between Ti foil and Ti counter electrode was 2 cm in all experiments.

To create periodic modulation of porosity across thickness of anodic titania film, a specific voltage profile was set as a staircase function of electric charge spent during anodizing using lab-made software. U(Q) anodizing profile was realized using the following algorithm:

- 1) At the initial stage (Q = 0 C), the anodizing voltage was set to 40 V.
- 2) After a short time interval Δt (ca. 30 ms), the increment of charge ΔQ was calculated by numerical integration of measured current. New value of charge $Q(t + \Delta t)$ is the sum of the charge value Q(t) at previous step and the increment ΔQ . Then the voltage was set to the new value $U(Q(t + \Delta t))$, which corresponded to the value of charge spent during anodizing in accordance with required voltage charge

profile.

3) The steps described in item #2 were repeated until the charge spent during anodizing became higher than the maximum value of charge in *U*(*Q*) profile. Finally, DC power supply was switched off.

Ti was anodized at the voltages in the range from 40 to 60 V using sine wave U(Q) profiles:

$$U = 50 + 10 \cdot \sin\left(\frac{2\pi Q}{P} - \frac{\pi}{2}\right),$$
 (1)

where P is the electric charge spent during one cycle of anodizing.

Four samples with charge density per cycle of 0.177, 0.213, 0.256, and 0.295 C·cm⁻² were obtained (denoted as S1, S2, S3, and S4, respectively). The total charge density spent during anodizing of each sample S1–S4 was 17.7 C·cm⁻². Sample S5 with charge density per cycle of 0.426 C·cm⁻² was prepared similar to the sample S2 with the same sine-wave increase and decrease in voltage in U(Q) profile, but with the additional constant voltage anodizing at 60 V for 0.213 C·cm⁻² in each cycle (Fig. 1a). The anodized area for all samples was 1.13 cm². After the end of anodizing the porous oxide films were washed in ethanol and then dried in air.

The morphology characterization of ATO films was performed by scanning electron microscopy (SEM) using LEO Supra 50 VP instrument. Perkin Elmer Lambda 950 spectrophotometer was used to record reflectance spectra at incident angle of 8°. The size of the light spot was $3 \times 3 \text{ mm}^2$.

3. Results and discussion

Electrochemical responses recorded during anodizing of titanium under cyclic voltage versus charge modulation are shown in Fig. 1. It can be clearly seen that the voltage applied to the electrochemical cell coincides well with the desired sine-wave U(Q) anodizing profile (Fig. 1a). The periodic variation of anodizing voltage between 40 and 60 V leads to the cyclic change of current density (Fig. 1b). Current density, *j*, hits the maximum and minimum values at the edges of the



Fig. 1. Electrochemical responses recorded during anodizing of titanium. (a) Applied voltage versus charge modulation U(Q) of the samples S1 (blue solid), S2 (cyan dash), S3 (green dot), S4 (red dash dot), and S5 (black solid). (b) Dependences of current density on voltage with different cycle number for the sample S2: 3 (black solid), 25 (red dash), 50 (green dot), 75 (blue dash dot). Inverse of current density (j^{-1}) versus charge density (q) is plotted in panels (c) and (d): data for the cases of potentiostatic anodizing at 40 V (orange solid) and 60 V (violet dot). Data for the samples S1 (blue solid), S4 (red dash dot) and linear approximation of j^{-1} maxima for the sample S4 in the case of $q \ge 0.5 \text{ C·cm}^{-2}$ (green dash line) are shown in panel (c); data for the samples S2 (cyan dash) and S5 (solid black) are given in panel (d). Thickness of the oxide films is calculated as a ratio of q to the experimental value of specific charge density. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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