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Fabrication of anodic aluminum oxide with incorporated chromate ions

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ABSTRACT

The anodization of aluminum in 0.3 M chromic acid is studied. The influence of operating conditions (like anodizing voltage and electrolyte's temperature) on the nanoporous anodic aluminum oxide geometry (including pore diameter, interpore distance, the oxide layer thickness and pores density) is thoroughly investigated. The results revealed typical correlations of the anodic alumina nanopore geometry with operating conditions, such as linear increase of pore diameter and interpore distance with anodizing voltage. The anodic aluminum oxide is characterized by a low pores arrangement, as determined by Fast Fourier transforms analyses of the FE-SEM images, which translates into a high concentration of oxygen vacancies. Moreover, an optimal experimental condition where chromate ions are being successfully incorporated into the anodic alumina walls, have been determined: the higher oxide growth rate the more chromate ions are being trapped. The trapped chromate ions and a high concentration of oxygen vacancies make the anodic aluminum oxide a promising luminescent material.

1. Introduction

Anodic aluminum oxide (AAO) forms hexagonally arranged arrays of nanopores during anodization [1]. The most common electrolytes applied in anodization of aluminum are sulfuric acid [2–11], oxalic acid [3,12–16] and phosphoric acid [3,17–21]. A type of electrolyte determines voltage range where anodization can be effectively conducted. An increase of pore diameter and interpore distance with anodizing voltage is linear for all of the applied electrolytes [6,12,13,19]. For this reason self-organized nanoporous alumina is a suitable template material for nanofabrication [22]. Moreover, nanopores diameter can be changed during anodization by rapid voltage change [23]. So formed alumina templates allows to obtain more sophisticated nanostructures [23].

According to Wernick et al., the anodization in diluted chromic acid can be successfully conducted at temperature range from 35 to 40 °C and voltage range from 0 to 50 V [24]. Parkhutik et al. has reported successful anodization performed in 0.2 M chromic acid and chromic acid–sulfuric acid mixture, in a galvanostatic mode, at current densities ranging from 0.5 to 10 mA/cm^2 and at 20 °C [25,26]. It was reported, that during growth of the anodic oxide, different electrolyte's anions are being incorporated in the AAO structure depending on a type of electrolyte [1]. The highest amount of the incorporated anions was observed for the oxide formed during anodization conducted in sulfuric acid, however, electrolyte's anions were also present in anodic porous alumina formed in phosphoric, oxalic and chromic acid [1]. The anodization in chromic acid resulted in the incorporation of chromate ions, whereas the anodization performed in sulfuric acid led to the incorporation of sulfate ions [25,26]. When aluminum was anodized in a mixture of chromic and sulfuric acid both species were detected in the AAO walls, what has been confirmed by X-ray photoelectron spectroscopy (XPS) [24].

Anodic aluminum oxide is also an interesting luminescent material. Its luminescent properties are acknowledged to factors like pores arrangement or type of anions incorporated into the AAO structure. Rauf et al. has reported the influence of anodizing voltage on PL spectra from the AAO formed in 0.3 M oxalic acid [27]. F$^+$ centers (oxygen vacancy with one electron) and F centers (oxygen vacancy with two electrons) present in AAO are responsible for PL bands at wavelength range 355–395 nm and 450–500 nm, respectively. Reported anodizing voltage was ranging from 40 to 70 V. The best AAO arrangement is for one formed at 40 V. Voltages increase spoils the AAO arrangement and increases a number of defects in the anodic oxide. Consequently, a number of excitation centers increases with anodizing voltage and also peak's position shifts towards greater wavelengths [27]. Furthermore, an electrolyte's concentration influences the PL of AAO [28]. The highest PL intensity was found for the AAO formed in the most concentrated electrolyte. The greatest F to F$^+$ PL intensity ratio was found for the

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AAO formed in 0.4 M oxalic acid [28]. Vrublevsky et al. attributed PL peak at 480 nm to the oxalate ions [29]. The oxalate ion exists in the AAO as a quite stable chelate compound. The band is present even after the AAO heat treatment up to 500 °C. Mukhurov et al. reported studies of PL of AAO formed in sulfuric acid [30]. There, the photoluminescence was attributed to F, F^+, F_2, $F_2{}^+$ and $F_2{}^{2+}$ centers. The divacancies are responsible for PL at near-UV and visible wavelengths [30]. Application of oxalic and sulfuric acid mixture as electrolyte for aluminum anodization allows to tune the PL of the prepared AAO [31,32].

The main goal of the paper is to fabricate the chromium doped AAO template for luminescent applications. The study is concentrated around the determination of voltages and temperatures of the anodization conducted in 0.3 M chromic acid where chromate anions are incorporated in the anodic aluminum oxide. A high chromic acid concentration was applied in order to increase an amount of the chromate ions luminescent centers. The determination of optimal experimental conditions in this electrolyte for achieving a maximal ions trapping have been undertaken. The influence of operating conditions on the nanopores geometry, including pore diameter, interpore distance, oxide layer thickness and pore density was also studied in details.

2. Experimental

A high-purity annealed aluminum foil (99.9995%, Puratronic, Alfa Aesar) was cut into coupons (0.5 cm × 2.5 cm) and degreased in acetone and ethyl alcohol. Subsequently, the samples were electropolished for 1 min at current density 0.5 A/cm^2 in a mixture of ethanol and perchloric acid (4:1 volumetric ratio). Platinum grid with surface area of 6.0 cm^2 was used as a cathode. The electropolishing process was conducted in a double walled electrochemical cell equipped with a powerful refrigerated circulator bath (Hueber) at 10 °C. Immediately after the electropolishing, the samples were rinsed twice in ethyl alcohol and deionized water. Next, the samples were coated with acid resistant paint and samples working area was limited to 0.5 cm^2. Anodic aluminum oxide (AAO) was formed by two-step self-organized anodization in 0.3 M chromic acid. Anodizations were conducted at four various voltages ranging from 20 to 50 V and four different temperatures ranging from 20 to 50 °C. After first one hour long step of anodization, the formed oxide was removed by chemical etching in a stirred mixture of 6 wt% H_3PO_4 and 1.8 wt% H_2CrO_4 at 60 °C. Next, the samples were re-anodized at the same set of experimental conditions, as used in the first step of anodization.

Geometry characterization was done with a high-resolution field emission scanning electron microscope (FEI, Quanta 3D FEG). Quantitative image analyses were done with NIS-Elements software purchased from Nikon and WSxM software [33,34]. Average pore diameter and pore density (number of pores occupying area of 1 μm^2) were measured with NIS-Elements from six top-view images of a given sample. Interpore distance was estimated from radial average of fast Fourier transformation images with WSxM software. Oxide layer thickness was measured from cross-sectional images of the samples.

Chemical composition of the anodic aluminum oxide was measured by use of the FE-SEM (FEI, Quanta 3D FEG) equipped with energy depressive X-ray spectrometer (EDS) at voltage of 30 kV.

The photoluminescence spectra were taken with FL 900 spectrofluorimeter (Edingurgh Instruments) with Xe lamp, using front-surface measurement mode. The excitation spectra were taken from 250 to 400 nm and emission spectra from 260 to 550 nm what allowed to evaluate photoluminescence excitation-emission maps.

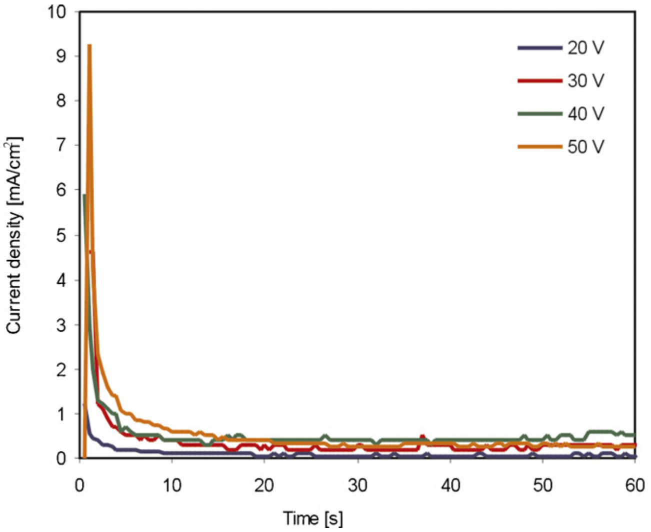

Fig. 1. Current density evolution during first 60 s of the second step of aluminum anodization in 0.3 M chromic acid at 30 °C.

Absorption spectrum of the aqueous solution of chromic acid was taken with UV–vis Cary spectrophotometer (Varian Company) at wavelength range from 250 to 550 nm.

3. Results and discussion

Fig. 1 shows current density evolution in time for aluminum anodized in 0.3 M chromic acid at 30 °C (Fig. 1). The greater the anodizing voltage, the higher the value of current density. For all of the studied electrolyte temperatures the same dependence was observed (Fig. 2). Furthermore, current density increases with temperature (Fig. 2). For example, aluminum anodized at 30 V at temperature of 20 °C is being oxidized with current density of 0.77 ± 0.16 mA/cm^2, whereas the anodization conducted at 50 °C occurs with current density of 7.33 ± 0.49 mA/cm^2. Anodiziation is a typical faradic process, so the greater the current density, the higher the amount of anodic oxide is being formed. Thus, the increase of temperature or anodizing voltage translates into the thicker anodic oxide layer (Fig. 3). The thinnest oxide layer of 0.76 ± 0.01 μm was measured for voltage of 20 V and temperature

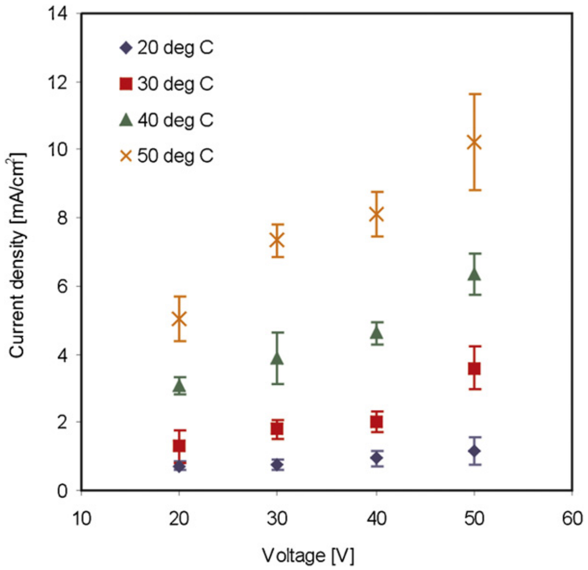

Fig. 2. Current density vs. anodizing voltage for anodization in 0.3 M chromic acid.