Thin Solid Films 519 (2011) 3516–3521

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Photoluminescent properties of barrier anodic oxide films on aluminum

S. Stojadinovic [a], *, R. Vasilic [b], Z. Nedic [c], B. Kasalica [a], I. Belca [a], Lj. Zekovic [a]

[a] *Faculty of Physics, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia*
[b] *Faculty of Environmental Governance and Corporate Responsibility, Educons University, Vojvode Putnika bb, Sremska Kamenica, Serbia*
[c] *Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia*

ARTICLE INFO

Article history:
Received 22 June 2010
Received in revised form 30 December 2010
Accepted 5 January 2011
Available online 22 January 2011

Keywords:
Photoluminescence
Barrier oxide films
Aluminum
Citric acid
Annealing
Anodization

ABSTRACT

We have investigated the photoluminescence (PL) spectra of barrier anodic oxide films on aluminum, formed in citric acid and in boric acid + borax. Strong PL bands are present in spectra of both electrolytes, featuring two distinct peaks in the 300 nm to 600 nm range. The first one is centered at about 460 nm, while the other peak shifts with the excitation wavelength. The PL intensity increases upon annealing, reaching the maximum value at about 500 °C. Experimental results indicate that the PL originates from optical transitions in two kinds of centers which are related to oxygen vacancies, F^+ and F. In addition, the PL of oxide coatings formed under anodic spark deposition was performed and a third peak at around 327 nm was observed.

1. Introduction

Two types of anodic oxide films can be formed during the anodization process of aluminum sample: barrier oxide films and porous anodic oxide films. The compact barrier oxide films on aluminum are formed by anodization (mostly under constant-current conditions) in electrolytes that possess significant buffering capacity and do not dissolve oxide at all (examples are: neutral boric acid, ammonium borate, ammonium tartrate, citric acid, tartaric acid, malic acid, succinic acid, etc.) [1,2]. They are produced at both aluminum/oxide and oxide/electrolyte interfaces as a result of the migration of O^{2-}/OH^- and Al^{3+} ions across the oxide, and assisted by a strong electric field. During the anodization, small amounts of anionic components of electrolyte are incorporated into the oxide at the oxide/electrolyte interface. Barrier oxide films are amorphous, have ionic conductivity and high electrical resistance. Their thickness is limited to several hundred nanometers; this is due to dielectric breakdown under strong electric field, followed by intense generation of spark discharges over the coating surface and accompanied by gas evolution. Oxide coatings formed at breakdown sites under anodic spark deposition contain crystalline and amorphous phases with constituent species derived from both metal and electrolyte [3].

Porous oxide films are formed in electrolytes which partially dissolve oxide (oxalic acid, sulfuric acid, phosphoric acid, etc.) and they consist of two regions: an outer region of thick porous-type aluminum oxide, and a thin, compact inner region adjacent to the metal [4]. The thickness of porous oxide films can grow up to hundreds of microns.

Anodic oxide films on aluminum exhibit many interesting properties which are enduring source of interest for researchers in various scientific and technological areas. One of these properties, photoluminescence (PL), is observed when anodic oxide films formed on aluminum are illuminated with ultraviolet radiation. PL has been investigated by many authors, but its nature and mechanism are yet to be completely understood. The intensity of the emitted PL radiation and shapes of the PL excitation and emission spectra depend on many factors, such as the nature of the electrolyte (organic or inorganic), conditions of the anodizing process [5], the thickness of oxide films [6] and their additional treatment (electrolytic or thermal) [7], wavelengths of the incident radiation [8], etc. PL spectral measurements can be used to determine refractive index, thickness and porosity of oxide films as well [9–12].

Most researchers have focused their attention to the PL of porous oxide films formed in oxalic, sulfuric and phosphoric acid. Generally, there are two opinions on the nature of PL centers in porous oxide films formed in organic electrolytes (i.e. oxalic acid). According to the first one, PL centers are defect centers related to oxygen vacancies [13]. The second opinion suggests that the PL could be attributed to oxalic impurities incorporated in oxide films during the anodization [14]. The origin of the PL from porous anodic films formed in inorganic electrolytes (sulfuric acid and phosphoric acid) is unclear. Usually, the PL from porous anodic films in inorganic electrolytes is simply considered to have the same origin as in films formed in oxalic acid [13]. G.S. Huang et al. identified two types of PL bands [15]. One is the

---

* Corresponding author. Tel.: +381 11 2630152; fax: +381 11 3282619.
E-mail address: sstevan@ff.bg.ac.rs (S. Stojadinovic).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.01.188

band with the emission center at about 460 nm, which is related to oxygen vacancies in porous oxide films. The other band is attributed to radiative recombination of carriers in isolated hydroxyl groups at the surface of the pore wall, whereas the photogeneration of carriers takes place in oxygen vacancies in the pore wall.

In spite of numerous articles investigating the PL of anodic oxide films (mainly porous) formed in various electrolytes, there is a deficiency of data on the PL spectra of barrier anodic oxide films. This is probably due to the weak PL intensity of thin oxide films, combined with effects such as reflection from anodic oxide/aluminum interface, which can influence PL spectra behavior. The aim of this work is to investigate the PL properties of barrier oxide films formed in organic electrolytes (citric acid) and compare them to the PL properties of barrier oxide films formed in inorganic electrolytes (boric acid + borax). The wavelength dependent PL and influence of thermal treatment on the PL are investigated. The nature of PL centers is discussed based on experimental data.

2. Experimental details

High purity cold-rolled aluminum samples (99.999%; Goodfellow) of dimensions 30 mm × 10 mm × 0.25 mm were used as starting material. Before anodization, aluminum was degreased in acetone, using ultrasonic cleaner, and then annealed for 4 hours in atmospheric conditions at 450 °C, to remove mechanical stresses and to recrystallize the aluminum. The anodic oxidation process was conducted under a constant current density of 15 mA/cm^2, at 17 °C, in 0.01 M citric acid, and in 0.01 M boric acid + 0.005 borax. Platinum wires were used as cathodes. During anodization, the electrolyte circulated through the chamber–reservoir system and temperature of the electrolyte was maintained within 0.1 °C. The electrolyte was prepared by using double distilled and deionized water and PA (pro analysis) grade chemical compounds. After anodization, the samples were rinsed in distilled water to prevent additional deposition of electrolyte components during drying.

PL spectral measurements were taken on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer, with a Xe lamp as the excitation light source and at room temperature. The obtained spectra were corrected for the spectral response of the measuring system and spectral distribution of the Xe lamp. The crystallinity of samples was analyzed by X-ray powder diffraction (XRD), using a Phillips PW 1050 powder diffractometer in Bragg-Brentano geometry, with Ni-filtered CuK$_\alpha$ radiation ($\lambda = 1.54178$ Å). Diffraction data were acquired over scattering angle 2θ from 10° to 90° with a step of 0.050° and acquisition time of 1 s/step. Infrared transmission spectra were studied using attenuated total reflection infrared Fourier transform (ATR-FTIR) spectroscopy (ThermoNicolet Avatar 370 FT-IR). The morphology of samples was characterized using an atomic force microscope (AFM; Veeco Instruments, model Dimension V). Micrographs were obtained in tapping mode under ambient conditions, using TAP300 tips (resonant frequency 300 kHz, force constant 40 N/m).

3. Results and discussion

A typical voltage versus time curve during aluminum anodization in citric acid is shown in Fig. 1. A relatively uniform growth of the compact barrier oxide film at a constant current density is characterized by a linear increase in anodization voltage [1,2]. This stage is followed by an apparent deflection from linearity in the voltage versus time curve, starting from the so-called breakdown voltage. The morphology of the oxide surface before and after breakdown is shown in Fig. 2. After the breakdown, the oxide surface becomes laced with a number of cracks, pores and channels.

The PL emission and corresponding excitation spectra of barrier oxide films formed by aluminum anodization of up to 450 V in citric acid are shown in Fig. 3. Wide PL bands are present in the 300 nm to 600 nm range. The intensity and the peak positions of emission and excitation spectra change with excitation and emission wavelengths, respectively. Two spectral peaks are observed in both emission and excitation PL spectra. Fig. 3a shows that, for all emission spectra, one spectral peak remains at a constant wavelength of about 460 nm, while the other peak shifts from about 425 nm to 470 nm, depending

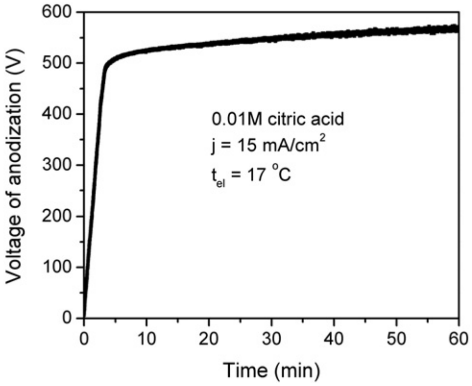

Fig. 1. Voltage–time dependence during galvanostatic anodization of aluminum in 0.01 M citric acid ($j = 15$ mA/cm^2, $t_{el} = 17$ °C).

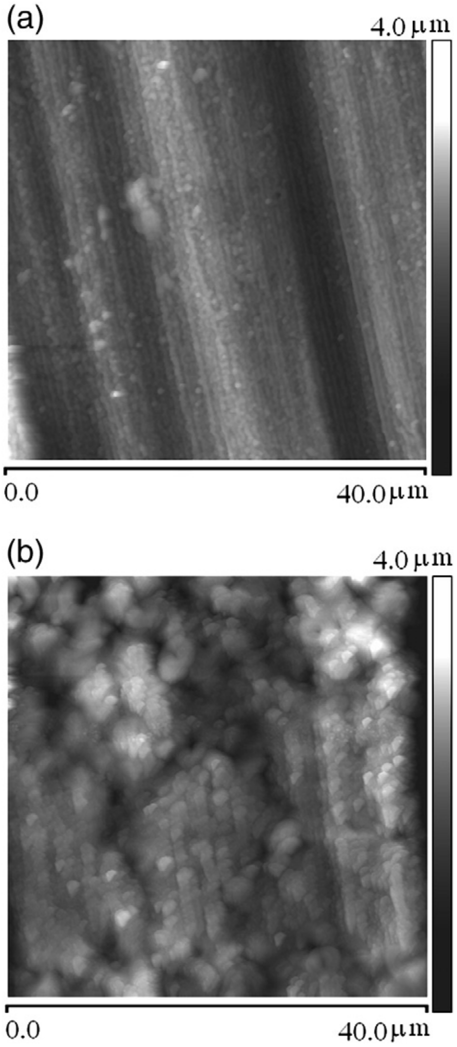

Fig. 2. AFM images of oxide films formed in 0.01 M citric acid: (a) before breakdown for anodizing voltage of 450 V (anodization time 3 min); and (b) after breakdown (anodization time 10 min).