Spectrochimica Acta Part A 81 (2011) 672–678

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Identification of the $C^2\prod$–$X^2\Sigma^+$ band system of AlO in the ultraviolet galvanoluminescence obtained during aluminum anodization

Mirjana Sarvan[a], Miljenko Perić[b], Ljubiša Zeković[a], Stevan Stojadinović[a,*], Ivan Belča[a], Marija Petković[a], Bećko Kasalica[a]

[a] Faculty of Physics, University of Belgrade, Studentski trg 12, Belgrade, Serbia
[b] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12, Belgrade, Serbia

ARTICLE INFO

Article history:
Received 19 April 2011
Received in revised form 27 June 2011
Accepted 28 June 2011

Keywords:
Galvanoluminescence
Anodization
γ-Alumina
AlO
OH

ABSTRACT

The first galvanoluminescence spectrum in the ultraviolet region obtained during anodization of high purity aluminum samples annealed at temperature above 525 °C is presented. An intense broad peak with the maximum at about 31,900 cm^{-1} is assigned to the transitions (some of them heretofore unobserved) between vibrational levels of the $C^2\prod \to X^2\Sigma^+$ spectral system of AlO, partly overlapped with the $A^2\Sigma^+ \to X^2\prod$ system of OH.

1. Introduction

Oxide films formed by anodization of aluminum exhibit many interesting properties, which are enduring source of interest for researchers in various scientific and technological areas. One of these properties, galvanoluminescence (GL), is a common name for emission of a weak electromagnetic radiation, mostly in the visible spectral region, during anodization of aluminum in suitable electrolytes [1,2]. This phenomenon has been investigated by many authors, but explanations of the nature and the mechanism of GL are still not completely resolved because of complex environment and many experimental parameters that determine the intensity and spectral distribution of GL. There are to main reasons for investigation of GL: The first one is that it (combined with other kinds oh measurements) yields information about the system considered, particularly about the microstructure of the oxide films formed in the process of anodization. The second reason is that the discharge built in course of this process is a convenient medium for occurrence of a number of spectral lines and bands and thus it can serve as a source of new spectroscopic information.

During the past several years, our group conducted a number of investigations of the GL [3–12] and showed that the nature and the intensity of GL depended on many factors such as type of electrolytes (organic or inorganic), surface pretreatment and anodizing conditions. Surface pretreatment of aluminum samples (surface preparation and annealing) has a significant influence on GL obtained in inorganic electrolytes [3,5,6]. In fact, the pretreatment of the samples governs the concentration of flaws ("flaws" is a general term for microfissures, cracks, local regions of different compositions and impurities, etc.) in oxide films, which are related to the GL mechanism. The annealing temperature of the samples is another pretreatment factor that affects the GL intensity [3–6]. Higher annealing temperature results in higher GL intensity. Annealing at different temperatures has different influences on the state of a sample's surface, number of defects, crystal grains and their orientation, in other words, on the concentration of flaws. We showed in our previous studies [3–5,7,10] that the GL spectra of oxide films formed in inorganic electrolytes had two spectral peaks in visible region. The first one was at about 23,300 cm^{-1}, and the second shifted from 16,700 cm^{-1} to 14,700 cm^{-1} with increasing voltage of anodization. In organic electrolytes, carboxylate ions incorporated in the oxide films during the anodizations acted as the GL centers [8], [9]. GL in organic electrolytes was attributed to deexcitation of the GL centers excited by electrons of the electron avalanche formed in a high electric field (nearly 10^7 V/cm) during aluminum anodization. We showed that the GL spectra obtained in organic electrolytes had two dominant spectral peaks which position and relative intensity depended on the anodization voltage. The first one appeared at about 22,200 cm^{-1}, and the second was shifted from 20,400 to 17,200 cm^{-1} with increasing anodization voltage [8,9].

---

[*] Corresponding author. Tel.: +381 11 2630 152; fax: +381 11 3282 619.
E-mail address: sstevan@ff.bg.ac.rs (S. Stojadinović).

1386-1425/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2011.06.072

Our investigation of GL of oxide films formed by anodization of aluminum samples annealed at temperatures above 500 °C in both types of electrolytes showed that the sudden rise in the formation of gamma crystalline regions caused by aluminum annealing was strongly related to the appearance of GL and its intensity [11,12]. The GL intensity is about two orders of magnitude higher for samples annealed at 550 °C than for samples annealed below 500 °C. In our recent study [11] we recorded the GL spectra and observed six intense emission bands with peaks around 23,250 $\mathrm{cm^{-1}}$, 20,700 $\mathrm{cm^{-1}}$, 18,400 $\mathrm{cm^{-1}}$, 17,400 $\mathrm{cm^{-1}}$, 16,600 $\mathrm{cm^{-1}}$, and 15,400 $\mathrm{cm^{-1}}$. A semi-quantitative analysis based on literature data on simple molecular species involving the Al atom, as well as those atoms whose presence was possible under given experimental conditions (hydrogen, oxygen, etc.), showed that the sources of GL were molecules/radicals AlH, AlO, Al_2 and AlH_2, related to the formation of gamma alumina crystal islands at annealing temperatures above 500 °C.

In spite of numerous articles that have investigated GL of anodic oxide films formed in various electrolytes, there is a deficiency of data on the GL spectra in the ultraviolet region. The aim of this work is to interpret the GL spectrum in ultraviolet region of anodic oxide films formed on aluminum samples annealed at temperatures above 525 °C.

2. Experimental

In our experiment, anodic oxide films were formed on high purity (99.999%) cold-rolled aluminum samples of dimensions 25 mm × 10 mm × 0.12 mm. The anodic oxidation process was carried out in a thermostated electrolytic cell with flat quartz windows. Inert platinum wires were used as catodes. The optical detection system consisted of a quartz objective of focal distance 55 mm, a spectrograph and a CCD (Charge Coupled Devices) camera (“Hamamatsu”, CCD cheep, type C10151) as detector. The wavelength and sensitivity calibration were performed by a pen lamp and a hydrogen (D_2) lamp, respectively. In order to remove impurities from the aluminum sample, it was degreased in ethanol by using an ultrasonic cleaner and dried in a warm air stream. The aluminum samples were annealed for 3 h at temperature of 525 °C and after that the samples were slowly cooled. For aluminum anodization, we used water solutions of 0.1 M phosphorous acid. The analysis of the alumina surface was carried out by x-ray diffraction; it proves the appearance of crystalline alumina at the sample's surface after annealing. Visual detecting of the islands of γ-alumina, shown in Fig. 1, is possible by a scan electron microscope if the samples are prepared in mixture of phosphorus and chromic acid.

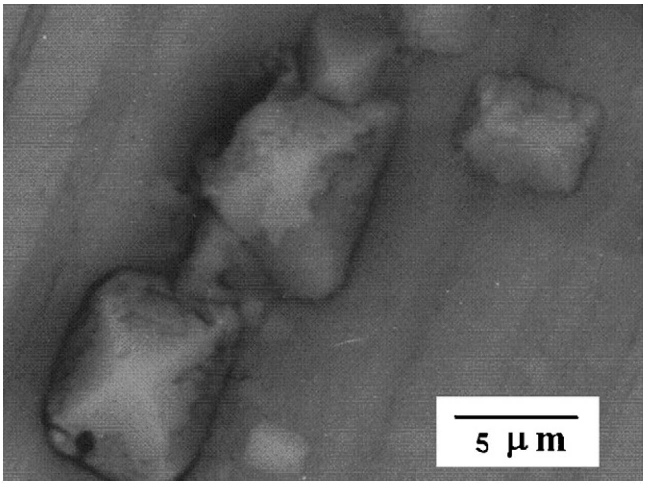

Fig. 1. SEM image of aluminum surface and islands of γ-alumina, obtained by thermal treatment (amplification of microscope 300 times).

3. Results and discussion

In our previous study [11] we investigated the spectral wavenumber range from 14,000 to 25,000 $\mathrm{cm^{-1}}$. We recorded a rich spectrum consisting of a series of narrow peaks we were able to interpret in terms of the transitions between several vibrational levels of the low-lying excited electronic states and those of the ground electronic state of several aluminum-containing, mostly diatomic species (AlH, AlO, Al_2, and AlH_2). No atomic lines, as well as no bands which could be assigned to molecular species not involving aluminum were detected. In the present work we extend our search to the wavenumber region from 25,000 to 45,000 $\mathrm{cm^{-1}}$. The sample was obtained during anodization of aluminum in phosphoric acid. Fig. 2 displays a spectrum obtained in the presence of alumina samples annealed at temperature of 525 °C. The striking difference between the spectrum shown in Fig. 2 and that recorded in our previous study is that in the present case we obtain several broad peaks with hardly visible structure; the most intense of them extends between 31,400 and 32,200 $\mathrm{cm^{-1}}$, with the maximum at about 31,900 $\mathrm{cm^{-1}}$. An inspection of the standard molecular data sources, like Refs. [13–16] shows that the only electronic system involving the above mentioned species (observed in the visible range in our previous study) is the $C^2\prod \rightarrow X^2\Sigma^+$ transition of AlO at 32,100–34,800 $\mathrm{cm^{-1}}$ [16]. However, the assignment of the observed feature to this transition is by no means unambiguous, because of the fact that the bands corresponding to the $A^2\Sigma^+ \rightarrow X^2\prod$ system of OH, whose presence cannot be excluded under given experimental conditions, appear in the same wavelength region. The most prominent band (0–0) of this electronic transition lies around 32,640 $\mathrm{cm^{-1}}$.

In the following, we shall concentrate on the most pronounced peak with the maximum at 31,900 $\mathrm{cm^{-1}}$. We carried out a series of experiments under the same conditions; the part of the spectrum between 31,400 and 32,200 $\mathrm{cm^{-1}}$ obtained in one of them is shown in Fig. 3a. The peak recorded in the framework of the present study is much too broad to be assigned to a single vibrational transition and seems to have a richer structure than that expected from a purely vibrational spectrum. In order to identify the structure of this peak we apply a smoothing procedure, based on the Savitzky–Golay method [17], implemented in the software package ORIGINE. The results obtained in this way for the original peak presented in Fig. 3a, are depicted in Fig. 3b.

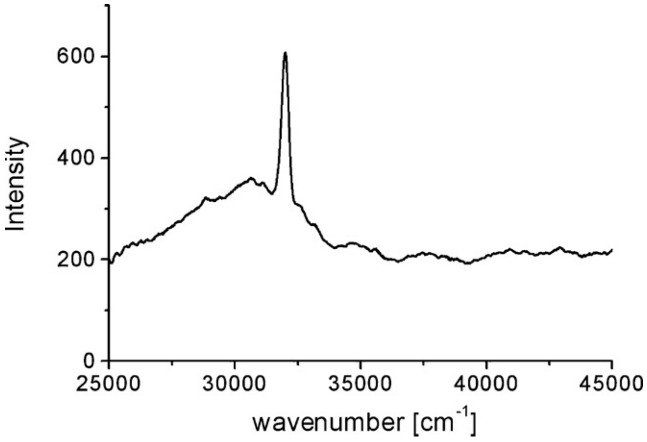

Fig. 2. Galvanoluminescence spectrum in the wavenumber region from 25,000 $\mathrm{cm^{-1}}$ to 45,000 $\mathrm{cm^{-1}}$.