



Electronic transitions during plasma electrolytic oxidation of aluminum

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ABSTRACT

In this article, we have presented our recent investigation of electronic transitions originating from barrier anodic oxide films under the conditions of plasma electrolytic oxidation in both organic and inorganic electrolytes. For the first time we have recorded luminescence spectra during electric breakdown and observed several intensive emission band peaks. Analysis based on literature data on atomic species whose presence is possible in this experimental setup showed that luminescence is related to electron transitions in atoms Al, O, H, Na. Furthermore, these results point to the same cause of optical radiation during aluminum anodization in inorganic and organic electrolytes under the breakdown conditions.

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1. Introduction

Barrier oxide films are commonly formed by anodization of aluminum samples in electrolytes which do not dissolve oxide film at all, e.g. water solutions of neutral boric acid, ammonium borate, ammonium tartrate etc. [1]. Their thickness is limited to several hundred nanometers due to dielectric breakdown initiation during film growth [2].

Oxide films formed by anodization of aluminum are the subject of intensive research due to its technological and industrial significance. Barrier type of layer has wide applications in industry of electrolytic capacitors, displays, in producing TFT in liquid crystal display devices, MIM cathodes for electron beam lithography systems etc. [3,4].

The anodic formation of barrier films of so-called valve metals can be carried out until the voltage attains a breakdown level, which we define as breakdown or sparking voltage. The presence of an electrolytic contact makes the breakdown features very peculiar and quite different from those of dry dielectric including metal/anodic film/metal system [5].

There were several attempts to develop the theory of electrical breakdown in oxide films on aluminum. Since the extensive studies of Gunthershulze and Betz [6], electrical breakdown during the anodization of valve metals has been the subject of many investigations. The idea that dielectric breakdown phenomena are due to electron ionization avalanches was theoretically developed by Rogowski [7] and Hippel [8] while the work of Joffe et al. [9] postulated an ionic conduction mechanism originated from ionization. Further reviews found difficulties in the definition of breakdown and also in interpretation of the processes [10–12].

The electrical breakdown process was generally explained as a consequence of an avalanche of electrons injected at the oxide/electrolyte interface [13]. Viji assumed, within this model, that the electrons were injected by a tunneling mechanism across the electrolyte/oxide barrier. Later, Yahalom [11] demonstrated the difficulty of the electrolyte to supply electrons. He postulated their existence from sporadic electron discharges at some definite points, which eventually develop into large-scale sustained avalanches.

One of the first attempts to develop a quantitative theory was made by Ikonopisov [14]. He proposed that electrons are injected in oxide conduction band by a Schottky mechanism and found out that this phenomenon depends on the nature of the anodized metal as well as composition and resistivity of electrolyte. Kalra et al. [15] observed the effect of electrolyte concentration, composition and resistivity on breakdown voltage in terms of Ikonopisov electron avalanche breakdown model and found that the major factor contributing to the decrease in breakdown voltage with increasing electrolyte concentration is the increasing primary electronic current.

Albella et al. analyzed the effect of the electron avalanches on the anodization voltage–time curves at constant current density [16,17] extending the Ikonopisov's model. Through the systematic studies using different concentrations of electrolytes they concluded that the primary sources of the avalanche electron current are the electrolyte species. They have shown that the energy gained by the collisions is 65 eV and it is high enough to ionize the atoms at rest.

The dielectric properties of insulators, and especially dielectric strength, strongly depend on defects. In the proposed model, the breakdown process starts with entries of the electrolyte species in the oxide as charged particles, anions, during the anodization process. These species, once incorporated into the oxide, behave as the impurity centers which can be ionized by applying a high-anodized field.

Freitas et al. [18] investigated the dependence of breakdown process of niobium oxide on the current density, the concentration

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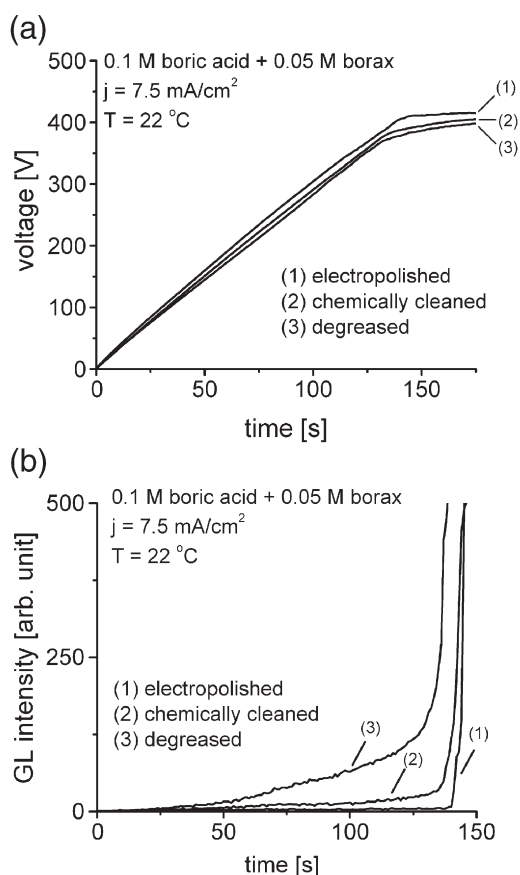


Fig. 1. Effect of the surface pretreatment on: a) voltage–time dependence; b) GL intensity–time dependence; during galvanostatic anodization of aluminum in 0.1 M boric acid + 0.05 M borax ($j = 7.5 \text{ mA/cm}^2$, $t_{el} = 22 \text{ }^\circ\text{C}$, $\lambda = 589 \text{ nm}$).

and the composition of the electrolyte and the time that the film is maintained under galvanostatic polarization. They determined that electrical breakdown is associated with small oscillations in the breakdown potential, the presence of sparks, anion incorporated in the film, and small holes in the film surface.

The aim of this work is to give some more contribution to the understanding of breakdown phenomena during aluminum anodization in electrolytes which form barrier oxide films (boric acid + borax and ammonium tartrate), by investigating luminescence under the breakdown conditions. It is well known that aluminum anodization in aforementioned electrolytes is followed by emission of weak optical radiation, mostly in the visible region of spectrum. This phenomenon

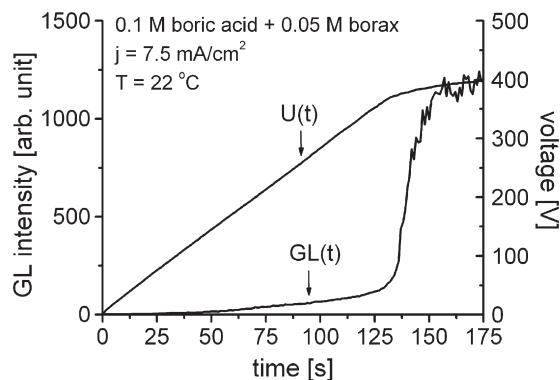


Fig. 2. Voltage–time and GL intensity–time dependence during galvanostatic anodization of aluminum in 0.1 M boric acid + 0.05 M borax ($j = 7.5 \text{ mA/cm}^2$, $t_{el} = 22 \text{ }^\circ\text{C}$, $\lambda = 589 \text{ nm}$).

is termed galvanoluminescence (GL) or electroluminescence [19,20]. GL of barrier oxide films is not the same in organic and inorganic electrolytes [21]. In organic electrolytes, GL is attributed to deexcitation of luminescence centers excited by electrons of the electron avalanche formed in a high electric field (nearly 10^7 V/cm) during anodization of aluminum [22,23]. GL centers are carboxylate ions incorporated in the oxide films during the anodization. On the other hand, in inorganic electrolytes, GL is correlated to the existence of “flaws” in the oxide films, generated probably by impurities from the surface [21,24]. We showed that the GL spectra of barrier oxide films have broad GL bands in the visible region [25,26].

As the anodization voltage approaches the breakdown voltage, a large number of sparks appear superimposed on the anodic GL. In this paper we have investigated the nature and source of additional optical radiation under the breakdown conditions.

2. Experimental

In the experiment, anodic oxide films were formed on high purity cold-rolled aluminum (99.999% obtained from Goodfellow) samples of $25 \text{ mm} \times 10 \text{ mm} \times 0.12 \text{ mm}$ dimensions. The surface of aluminum was prepared for anodization in three ways: (a) degreased in acetone by using ultrasonic cleaner; (b) chemically cleaned in the bath consisting of 20 g/L chromium trioxide and 35 ml/L concentrated phosphoric acid at $80 \text{ }^\circ\text{C}$ for 5 min followed by rinsing in distilled water and dried; (c) electropolished at a constant current of 100 mA/cm^2 below $10 \text{ }^\circ\text{C}$ for 4 min in an electrolyte containing perchloric acid (60 wt.%) and ethanol in a 1:4 ratio by volume.

The anodic oxidation process was carried out in an electrolyte chamber with flat glass windows. Platinum wires were used as cathodes. The electrolyte was thermostated at a certain temperature. The electrolyte circulated through the chamber–reservoir system, and the control temperature sensor was situated immediately by the sample. The temperature of the electrolyte was maintained during anodization to within $0.1 \text{ }^\circ\text{C}$. For anodization of aluminum we used water solution of 0.1 M boric acid + 0.005 M borax and 0.1 M water solution of ammonium tartrate. The electrolytes were prepared using double distilled, deionized water and PA grade chemical compounds.

For luminescence spectra measurement we used an optical-detection system consisting of a large-aperture achromatic lens, a Hilger spectrograph with diffraction grating 150 grooves/mm (wavelength range from 390 nm to 720 nm) and a very sensitive PI-MAX ICCD cooled camera with high quantum efficiency manufactured by Princeton Instruments. In order to get better resolution we replaced this grating with the one with 1200 grooves/mm, which allowed the recording of spectra in the wavelength range of 43 nm and obtaining better resolution. The CCD chip consisted of 1024×256 pixels, approximately $26 \mu\text{m} \times 26 \mu\text{m}$ each. To reduce the dark current, the CCD chip was cooled at $-40 \text{ }^\circ\text{C}$ using Peltier devices. The optical-detection system was calibrated using a LED-based light source [27].

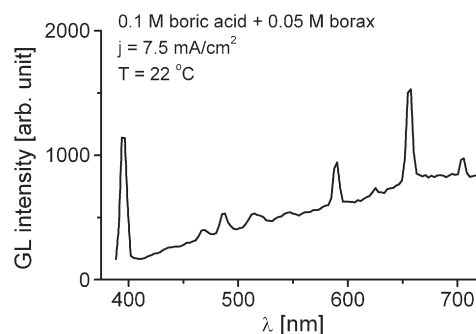


Fig. 3. GL spectrum recorded during the anodization of aluminum in 0.1 M boric acid + 0.05 M borax under breakdown conditions (grating of 150 grooves/mm) in the wavelength range from 390 nm to 720 nm.

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