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Photoluminescent behavior of heat-treated porous alumina films formed in malonic acid

I. Vrublevsky [a,*], A. Jagminas [b], S. Hemeltjen [c], W.A. Goedel [c]

[a] Department of Micro and Nanoelectronics, Belarusian State University of Informatics and Radioelectronics, 6 Brovka str, Minsk 220013, Belarus
[b] Institute of Chemistry, A.Goštauto 9, LT-01108 Vilnius, Lithuania
[c] Institut für Chemie, Technische Universität Chemnitz, D-09107, Germany

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ABSTRACT

In the present work IR spectroscopy, electron probe microanalysis (EPMA) and photoluminescence (PL) spectral measurements were applied to study the effect of treatment temperature (T) on compositional and luminescent properties of malonic acid alumina films. Our studies have shown that the heat treatment of anodic alumina films at investigated temperatures from 100 up to 700 °C changes their photoluminescence spectra considerably. An increase in T results in the PL intensity growth. When reaching its maximum at 600 °C the luminescence intensity then decreases drastically with further T growth. The films heat-treated at 500 and 600 °C demonstrate asymmetrical PL band with Gaussian peaks at 437 and 502 nm. We proved that the malonic acid species incorporated into the alumina bulk during the film formation are responsible for photoluminescence band with its peak at 437 nm.

1. Introduction

In recent years the optical properties of porous anodic alumina films with ordered porous structure have been the subject of intensive studies [1–7]. It is worth mentioning that such studies are mainly focused on interaction between the luminescent properties and changes in the amorphous structure of anodic alumina films [5,7]. However, though a great number of studies devoted to this topic have been made, the origin of blue photoluminescence (PL) remains unclear. This phenomenon used to be explained through two main points of view. The first one assigns the observed blue emission band to singly ionized oxygen vacancies (F^+ centers) [8,9]. Another point of view persists that oxalate impurities incorporated into the alumina bulk are transformed into the luminescent centers with a blue PL band around 470 nm during the film formation [2,10]. Some authors use the approach which includes these both viewpoints [7]. Assuming that the blue emission band in the PL spectra of anodic alumina films originates from the coactions of the singly ionized oxygen vacancies and luminescent centers transformed from oxalate impurities. Recently in a study of optical and luminescent properties of heat-treated oxalic acid alumina films [11] it has been shown that oxalate species incorporated into the alumina bulk are responsible for blue photoluminescent emission.

The present paper aims to study the influence of heat treatment on photoluminescence properties of malonic acid alumina films through a comparative analysis of their composition and PL since the heat treatment is known to allow changing the structure of species incorporated into the alumina bulk as well as properties of the transformed luminescent centers. The choice of malonic acid alumina films is mainly due to the fact that malonic as well as oxalic acid, belongs to dicarboxylic acids with the only difference in the methylene group. As these acids have a common nature it could be of scientific interest to compare the luminescent behavior of the malonic acid alumina films with that of the films formed in oxalic acid.

2. Experimental

Aluminum foil of 99.999 at.% purity, 10.0 μm thick, purchased from Goodfellow, was used in our experiments. The aluminum sheets cut from this foil were anodized from both sides in a 0.8 M malonic acid solution ($H_4C_3O_4$) under a constant current of 6.0 mA cm^{-2} for about 60 min (steady-state voltage of 102 V) until all aluminum was spent. Some part of the aluminum sheets was anodized from both sides in a 0.3 M oxalic acid solution $(COOH)_2$ at a constant voltage of 40 V for about 20 min until receiving a transparent view. During anodizing the electrolyte was vigorously stirred and its temperature was kept constant at 18 ± 0.1 °C with a Thermo Haake DC10 thermostat.

The cross-sections of two-sided porous alumina films, electrochemically formed in both the malonic and oxalic acid solutions,

* Corresponding author. Tel.: +375 17 2938024; fax: +375 17 2932333.
E-mail address: vrublevsky@bsuir.edu.by (I. Vrublevsky).

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were investigated using a scanning electron microscope (SEM) JOEL 840A.

Infrared data of porous alumina films were taken using a spectrometer Bruker IFS 48 FTIR in the transmission mode. The photoluminescence measurements were taken on a PerkinElmer fluorescence spectrophotometer. The heat treatment of specimens, if indicated, was carried out in an oven under an ambient atmosphere for 2 h.

All the solutions for these experiments were prepared from deionized water and reagent grade chemicals.

The composition of the anodic alumina films was determined with an electron beam microprobe Camera SX100 using an accelerating voltage of 15 keV and a beam current of 10 nA. In order to ensure the necessary accuracy of EMPA measurements 10 points were selected on the surface of each anodic alumina film and then an average value was calculated.

3. Results

Fig. 1 shows SEM micrographs of the cross-sections of the two-sided porous alumina film formed in the malonic acid solution during galvanostatic anodizing (a) and in the oxalic acid solution at a constant voltage (b). It can be seen from Fig. 1(a) that the film formed in malonic acid has a disordered pore structure while for the film formed in oxalic acid a highly ordered nano-pore array with a close-packed structure is observed.

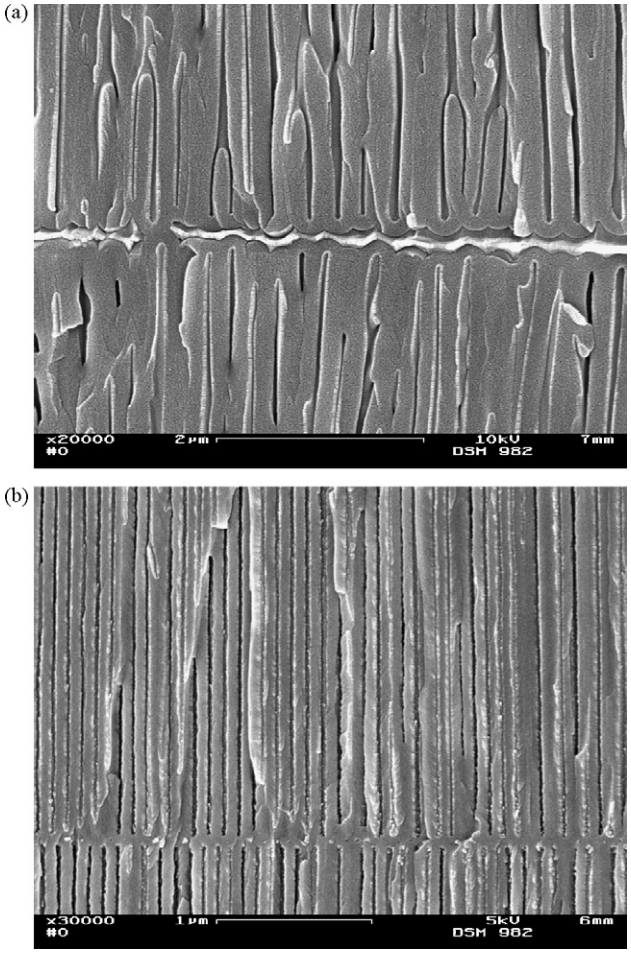

Fig. 1. SEM images showing cross-sections of porous alumina films formed by two-sided anodizing in a solution of malonic acid at constant current density of 6.0 mA cm^{-2} (a) and in a solution of oxalic acid at 40 V (b).

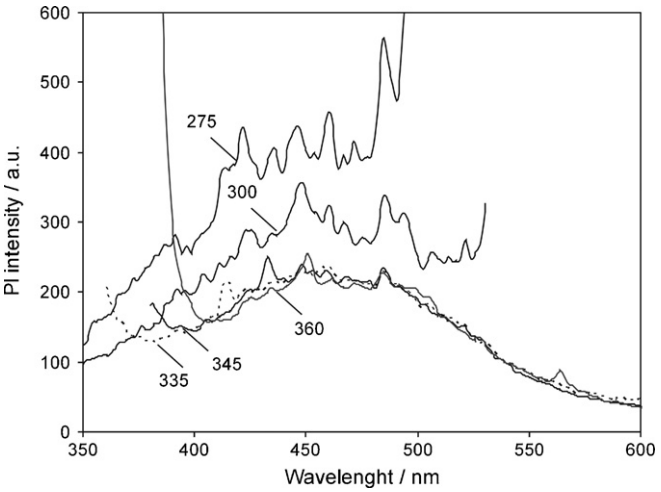

Fig. 2. Photoluminescence spectra of as-anodized anodic alumina films formed in malonic acid excited at different wavelengths, λ_{exc}.

Fig. 2 shows the PL spectra of as-anodized alumina films formed in malonic acid for different excitation wavelengths. It is evident that the broad emission band appears at about 330–600 nm. First, the intensity of the photoluminescence band decreases with an increase in the excitation wavelength from 275 to 335 nm, and remains almost unchanged at about 335–360 nm. Fig. 3 plots the photoluminescence spectra for the malonic acid alumina films heat-treated at temperatures up to 700 °C under a 335 nm excitation. It is obvious from Fig. 3 that the heat treatment of up to 300 °C leads to a negligible rise in the photoluminescence intensity while the films heat-treated above 300 °C demonstrate a visible increase in the PL. Heat treatment at 600 °C almost does not change the PL intensity in comparison with heat treatment at 500 °C. Heat treatment at higher temperatures reduces the photoluminescence intensity drastically. The spectra of the anodic films heat-treated at 500 and 600 °C do not have a clearly defined maximum, which is typically observed for one luminescent center. We can assume that the emission band originates from few luminescent centers. Therefore, it could be interesting to investigate the influence of the excitation wavelength (λ_{exc}) on the emission band behavior for this kind of anodic films. Fig. 4 plots

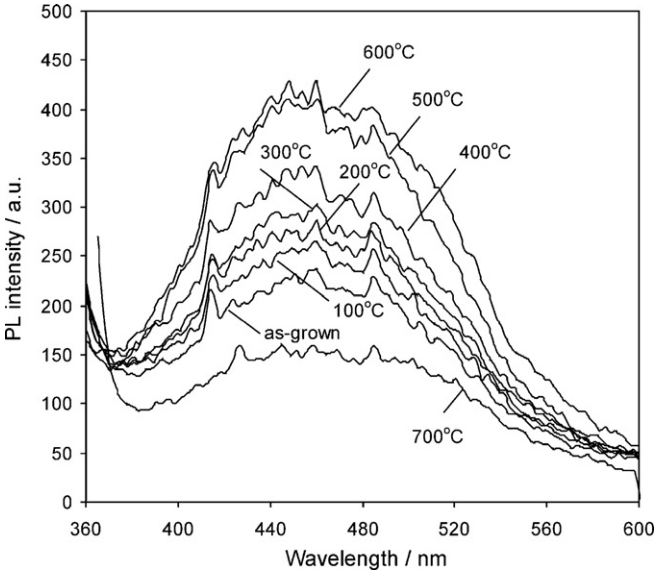

Fig. 3. Photoluminescence spectra of malonic acid alumina films heat-treated at indicated temperatures. λ_{exc} = 335 nm.