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Blue luminescence in porous anodic alumina films: the role of the oxalic impurities

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Abstract

Porous anodic alumina (PAA) films with ordered nanopore arrays have been prepared by electrochemically anodizing aluminium in oxalic acid solutions, and the role of the oxalic impurities in the optical properties of PAA films has been discussed. Photoluminescence (PL) measurements show that the PAA films obtained have a blue PL band with a peak position at around 470 nm; the oxalic impurities, incorporated in the PAA films during the anodization processes and already existing in them, could be being transformed into PL centres and hence responsible for this PL emission.

1. Introduction

Porous oxide growth on aluminium under an anodic bias, in various electrolytes, has been extensively studied for many years [1]. Owing to their unique pore structures, porous anodic alumina (PAA) films have been used as host materials to prepare nanostructures with a wide range of materials in recent years [2]. For example, with photoluminescent materials such as siloxenes [3] or Tb-doped titania xerogel [4] deposited into the pores of the PAA films, the nanocomposites obtained have shown novel photoluminescence (PL) properties. Furthermore, the application of PAA films with highly ordered nanopore arrays as two-dimensional photonic crystals [5] or micropolarizers [6] has been reported previously.

For studies of the interesting properties appearing for the nanocomposites or nanodevices related to PAA films, a complete understanding of the self-properties of the PAA films is very important and necessary. Investigations on PAA films formed in oxalic acid solutions have shown that these membranes have a blue PL emission band with a peak position around 470 nm [7, 8]. However, the PL mechanism and the PL centres are still not fully understood. For example, Yamamoto *et al* [7] have reported previously that the oxalic impurity incorporated in the PAA films during the anodization process is responsible for this blue luminescence.

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A different PL mechanism has been presented recently by Du *et al* [8], in which the singly ionized oxygen vacancies, F^+ centres, have been considered as the origin of the 470 nm PL emission band. These controversial interpretations suggest that further studies on the luminescence properties of PAA films are necessary.

We have prepared PAA films by anodizing aluminium in oxalic acid solutions and studied their optical properties. The investigation results reveal that the oxalic impurities play important roles in the luminescence properties of PAA films formed in oxalic acid solutions. Details are reported in this paper.

2. Experimental details

The PAA films used in this work were prepared in a two-step electrochemical anodization process [8]. High-purity (99.999%) aluminium foils were used as the starting material. Before anodization, the aluminium foils were first degreased with acetone, then annealed at 400 °C under vacuum conditions to remove mechanical stresses and allow recrystallization, and finally electropolished in a solution of perchloric acid and ethanol ($HClO_4:CH_3CH_2OH_5 = 1:9$ (vol), current density $0.3 A cm^{-2}$). Anodization was carried out in 0.3 M oxalic acid solutions and 0.3 M sulfuric acid solutions at 10 °C. The anodization voltage used for the oxalic PAA films (sample A) and the sulfuric PAA films (sample B) were 40 and 25 V, respectively. After the first anodization process, performed for 4 h, the alumina layer produced on the aluminium substrate was removed in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) solutions at 60 °C for 6 h, then the specimens were anodized again for 8 h under the same conditions as in the first step. After the two-step anodization, the aluminium substrate remaining at the bottom of the samples was totally removed by using a saturated $SnCl_4$ solution. Finally, the resulting PAA films were cleaned with de-ionized water several times, and dried at 80 °C for 5 h before characterization.

The morphology and structures of the PAA films obtained were characterized by using atomic force microscopy (AFM, AutoProbe CP), scanning electron microscopy (SEM, JEOL JSM-6300), transmission electron microscopy (TEM, JEM-200CX), and x-ray diffraction (XRD, D/MaxrA, Cu $K\alpha$, $\lambda = 0.1542$ nm) techniques. Fourier-transform infrared (FTIR) spectroscopy was performed on a Nicolet 170SX spectrometer. Optical absorption data were collected on a Cary 5E UV–visible–NIR photometer. PL spectra of the PAA films obtained were collected using a visible–ultraviolet spectrophotometer (HITACHI 850) with a Xe lamp as the excitation light source. X-band electron paramagnetic resonance (EPR, EPR-200) spectra were also measured. All these experiments were carried out at room temperature.

3. Results

3.1. Morphology and nanopore structures of PAA films

The geometrical characteristics of the as-prepared PAA films used in this work are as follows: about 12 mm in diameter and 30 μm in thickness. All the as-prepared samples are transparent. Sample A is light yellow in colour, while sample B is colourless.

It is well documented that the nature of the anodizing process is based upon the electrochemical principle that a current is passed through an electrolyte in which an aluminium anode is employed [1]. When an acid solution (usually oxalic, sulfuric, or phosphoric acid) is used, the PAA film obtained has pore diameters varying from 5 to 200 nm and lengths up to tens of microns. The bottom of each pore also consists of a thin, nonporous inner oxide layer adjacent to the substrate metallic aluminium (also called the barrier layer). A schematic

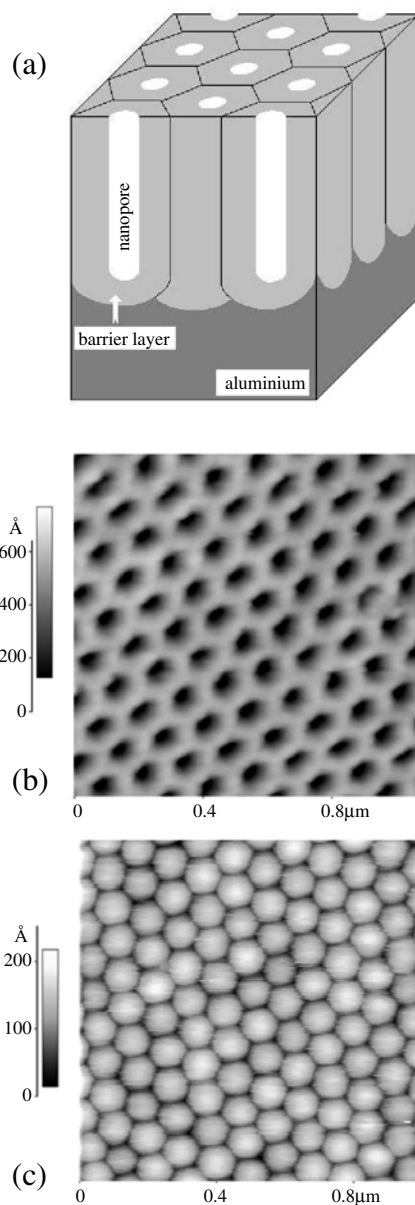


Figure 1. PAA film structures: (a) a schematic diagram, (b) an AFM top-view image, and (c) an AFM bottom-view image. The PAA films obtained in 0.3 M oxalic acid solution were used for AFM measurements.

diagram of the accepted PAA film structures [1, 9] appears as figure 1(a). The PAA film is presented as a close-packed network of hexagonal columns with rounded bottoms; this microstructural concept is derived from our AFM investigations (figures 1(b) and (c)). Further characterizations using SEM and TEM have shown that all the as-prepared PAA films possess highly ordered nanopore arrays arranged in a close-packed hexagonal pattern [1, 5, 8, 9]. The nanopore diameters and interpore spacings of the oxalic PAA films (sample A) are about 50 and 100 nm, respectively. The sulfuric PAA films (sample B) have the nanopore diameters

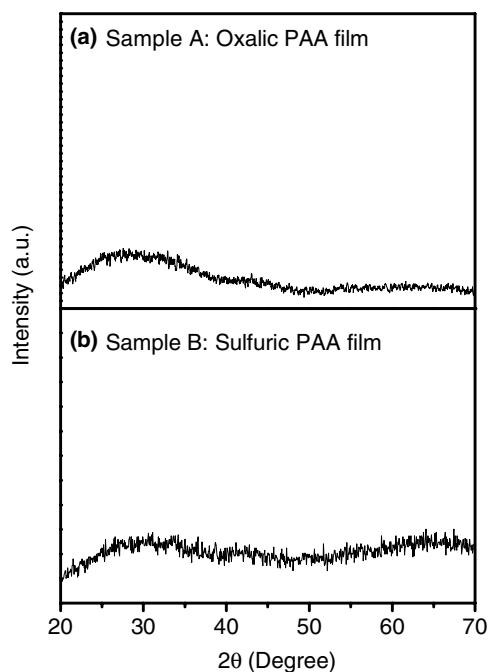


Figure 2. The XRD pattern of the as-prepared PAA films.

and intercore spacings of about 20 and 45 nm, respectively [8, 9]. Moreover, all the as-prepared samples are shown to be amorphous in nature (figure 2), as observed by using the XRD technique.

3.2. Structural characteristics of PAA films

The results from FTIR spectroscopy of the as-prepared sample A and sample B, along with those for the samples annealed at 400 °C in air, are shown in figure 3. H₂O molecular and/or –OH group stretching vibrations appear in the range of 2800–3700 cm⁻¹. The arising of a sharp peak at 2342 cm⁻¹ only appearing for sample A has been attributed to the formation of CO₂ inside the PAA films [3]. Comparing the adsorption spectroscopy of figure 3, we see that the adsorption peak of the CO₂ increases at a temperature of 400 °C; in this work, this has been attributed to the decomposition of the initial carboxylate species existing in the oxalic PAA films [7, 9–11] rather than the CO₂ from the air.

Figure 4 shows the optical absorption spectra of the PAA films obtained. The sulfuric PAA films (sample B) show no obvious absorption band from 250 to 360 nm. However, the oxalic PAA films (sample A) feature two absorption bands around 250 and 300 nm, which is similar to the case reported previously [12]. It can be seen that sample A has different optical absorption properties to sample B, revealing that the intrinsic structural characteristics of samples A and B are clearly different.

3.3. Photoluminescence (PL) of PAA films

Figure 5 shows the PL excitation and emission spectra of the PAA films in the ultraviolet-to-green region. Sample A shows an intensive and broad PL emission band peaked around

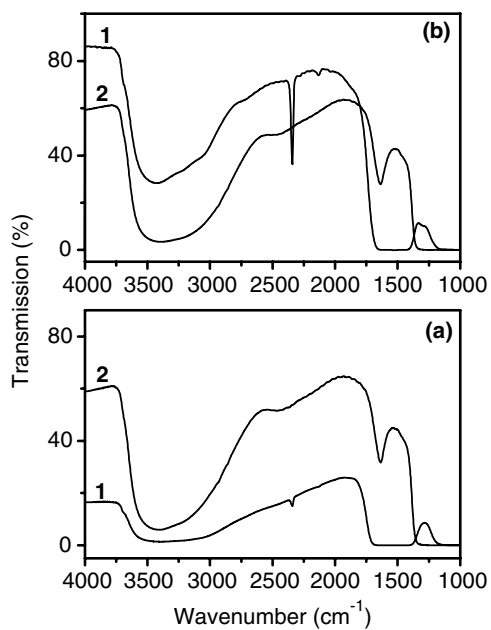


Figure 3. FTIR spectroscopy of (a) the as-prepared PAA films and (b) the samples annealed at 400 °C in air. 1 and 2 indicate the oxalic PAA film (sample A) and sulfuric PAA film (sample B), respectively.

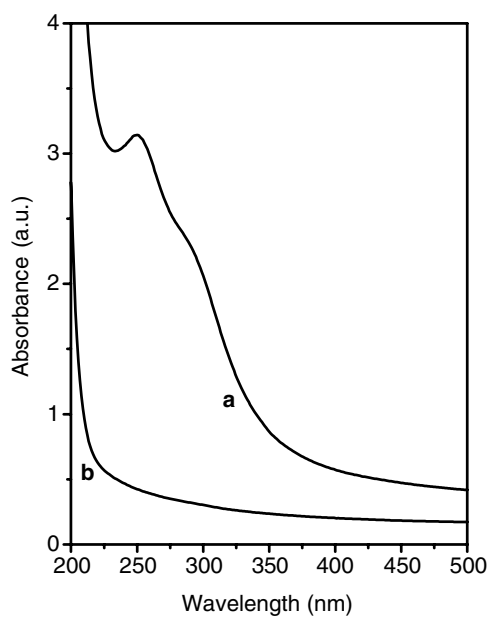


Figure 4. The optical absorption spectra of (a) the oxalic PAA film (sample A) and (b) the sulfuric PAA film (sample B).

470 nm [7, 8]. Monitoring the emission wavelength at 470 nm, a major excitation band around 360 nm and a weaker side band located around 250 nm were observed. For PAA

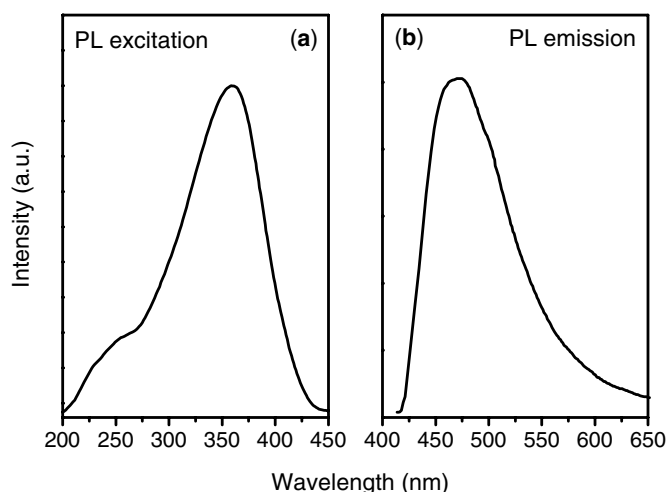


Figure 5. The PL excitation (a) and emission (b) spectra of the as-prepared oxalic PAA film (sample A). The monitored wavelength for (a) is 470 nm. The excitation wavelength and filter used for (b) are 360 and 430 nm, respectively.

films excited by using the two excitation wavelengths, only the 470 nm emission band, with different intensities, was observed. This suggested that the 470 nm emission is related to the two excitation centres.

The sulfuric PAA films prepared in this work have no obvious luminescence, which is at variance with previously reports [8, 13]. There are two possible reasons which should be considered. One is that the luminescence intensity of the sulfuric PAA films was very weak [8]. Another important factor considered in this work is that the blue luminescence of the oxalic PAA films would have a different origin from that of the sulfuric PAA films [7, 8, 13]. Since the physical or chemical properties of materials are strongly dependent on their components and structures, on the basis of the above-mentioned structural characteristics of PAA films (figures 3 and 4) we suggest that the F^+ centre [8, 13] is not suitable for interpreting the PL emission for both the oxalic and the sulfuric PAA films [8]. This assumption is discussed in detail in the following section of this paper.

4. Discussion

Recently, Wu *et al* [13] have reported that the PAA films formed in sulfuric acid solution have three PL emission bands with peak positions around 295, 340, and 395 nm. However, the PAA films prepared by Du *et al* [8] in sulfuric acid solution have only a very weak PL emission in the wavelength range from 400 to 600 nm. Although the luminescence characteristics of these sulfuric PAA films show great differences, F^+ centres have been used to explain these PL emissions in the two cases [8, 13]. This reveals that the luminescence properties of the PAA films are very sensitive to their chemical and structural characteristics, which depend mainly on their preparation conditions.

In this paper, we have found that the luminescence characteristics (such as the PL intensity) of the oxalic PAA films show clearly differences from those of sulfuric PAA films. It has been reported previously that oxalic impurities could be incorporated into PAA films [7, 9–11] during the anodization processes:

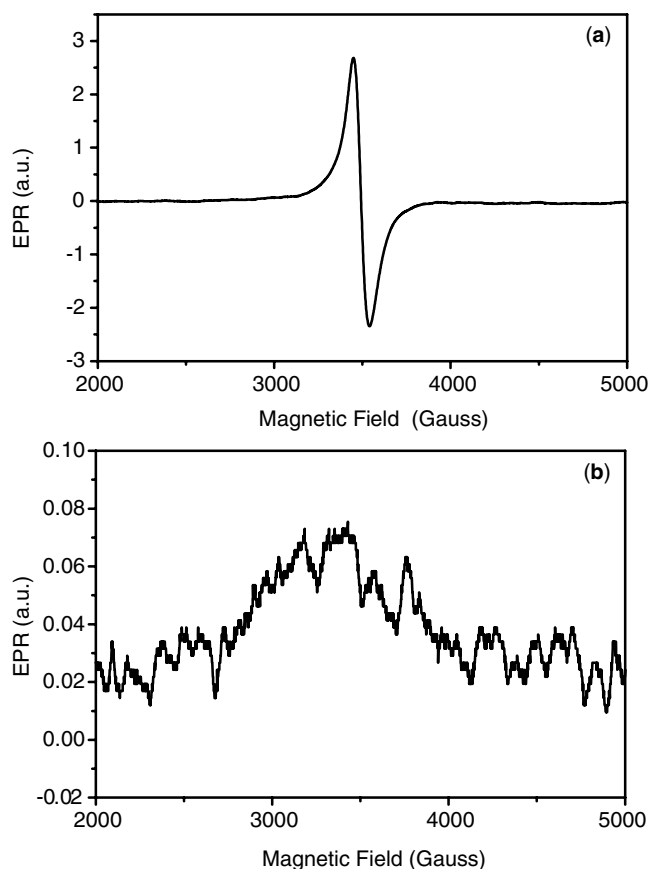


Figure 6. X-band (9.46 GHz) EPR traces of (a) the oxalic PAA film (sample A) and (b) the sulfuric PAA film (sample B) at room temperature.



The dissociation of acids generates conjugate base anions (reaction 2), and the conjugate base anions can partly replace the O^{2-} in the oxide formed (i.e. PAA), as substitution or contamination impurities within some depth [9–11]. It is reasonable to assume that the incorporated impurities existing in the PAA films would have important influences on their optical properties [7].

For studies on the PL properties of the PAA films, it should be established first whether the F^+ centres that are found in crystalline $\alpha\text{-Al}_2\text{O}_3$ [14] can also exist in amorphous PAA films or not. To the best of our knowledge, there has been no direct evidence, experimental or theoretical, for the existence of F^+ centres in PAA films until now. Furthermore, it has been shown by previous investigations that crystalline alumina (or sapphire) tends to be strongly stoichiometric, and it is extremely difficult to form anion vacancies in such materials [14]. The amorphous PAA films were prepared in oxy-acid solutions, and plenty of oxygen-containing matter such as H_2O , $\text{Al}_2\text{O}_3 \cdot n(\text{OH})$, and oxy-acid ions would be incorporated into the PAA films formed [1, 9–11]. How the oxygen deficiency defects (oxygen vacancies) can be produced in the oxygen-rich environment is a question requiring further investigation.

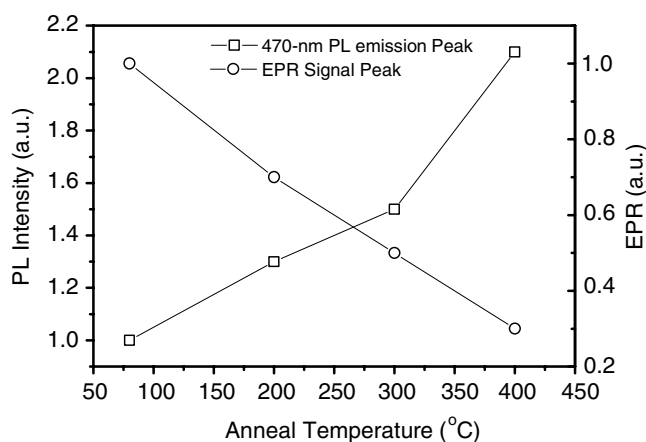


Figure 7. The intensity of the 470 nm PL emission peak (a) and the EPR signal of the oxalic PAA film as a function of annealing temperature. The data for the as-prepared sample (dried at 80 °C for 5 h) were treated as unit 1. All data were recorded at room temperature.

Previously, Du *et al* [8] have observed an EPR signal from the oxalic acid PAA films, which was thought to be evidence for the existence of singly ionized oxygen vacancies: F^+ centres in PAA films. We have characterized the PAA samples obtained by using the EPR technique, and observed the same EPR signal as was reported previously (figure 6). However, there are great differences between the two kinds of PAA film as regards the EPR spectrum shapes and signal intensities. Therefore, it is reasonable to attribute the EPR signal of the oxalic PAA films to oxalic impurities rather than F^+ centres [8]. This assumption is also supported by the following annealing treatment experimental results.

Figure 7 shows the 470 nm PL emission peak intensity, together with the intensity of the EPR signal peak for the oxalic PAA films as a function of annealing temperature. The annealing treatment was performed in air at different temperatures for 5 h. The 470 nm PL intensity increases with the rise of the temperature [8]; however, the EPR signal intensity decreases with the rise of the temperature. This reveals that the origin of the 470 nm PL emission is different from that of the EPR signal. Yamamoto *et al* [7] have reported previously that the oxalic ions can be incorporated into PAA films and decomposed by the high electric field set up inside the pores, or by the Joule heating. Then the oxalic impurities are expected to transform into intermediate compounds, and finally into PL centres, generating 470 nm PL emission. We suggest that the oxalic impurities incorporated within the oxalic PAA films would have different ‘existing’ and ‘distributing’ forms [7, 9], and, therefore, have different optical transition probabilities and activities (see figures 4 and 5). During the annealing treatment, the oxalic impurities incorporated would decompose. On the one hand, a large number of $=CO$ groups would form [3], resulting in the transmittance intensities of the 2342 cm^{-1} band enlarging (figure 3). On the other hand, with the increase of the annealing temperature, the number of PL centres generated from the decomposition of oxalic impurities would enlarge, resulting in the 470 nm PL emission intensities increasing (figure 7).

On the basis of the above discussion, we consider that the evidence for F^+ centres in oxalic PAA films is slight. The PL centres transformed from the incorporated oxalic impurities during the anodization process [7] are responsible for the 470 nm blue luminescence. However, the details of the oxalic impurities existing in the oxalic acid PAA films, such as their ‘existing’ and ‘distributing’ forms, are not very clear at present. Therefore, further investigations on the details of the PL properties of the PAA films are necessary.

5. Conclusions

In summary, we have prepared PAA films and investigated their PL properties. The experimental results and discussion presented herein reveal that the PL centres transformed from the incorporated oxalic impurities during the anodization process are responsible for the 470 nm blue luminescence.

Acknowledgments

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