



# Photoluminescence enhancement of nanoporous alumina using one-step anodization of high- and low-purity aluminum at room temperature



C.K. Chung\*, B.Y. Chu, C.H. Tsai, C.R. Hsu

Department of Mechanical Engineering and Center for Micro/Nano Science and Technology, Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 701, Taiwan, ROC

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## ABSTRACT

In this article, we investigate the enhanced photoluminescence (PL) behavior of nanoporous anodic aluminum oxide (AAO) formed by one-step anodization of aluminum (Al) in oxalic acid at room temperature (25 °C) from both high- (99.99%) and low-purity (99%) Al. Compared with studies using the traditional two-step direct-current anodization at low temperature (0–10 °C), we introduce hybrid-pulse anodization to synthesize AAO from high- and low-purity Al at 25 °C for enhancing the PL. The PL intensity of high-purity AAO was stronger than the low-purity one due to the reduced surface scattering and intrinsic impurity inhibition. Besides the purity effect, AAO formed at the elevated temperature of 25 °C also greatly enhanced the PL intensity compared to that at the low temperature of 5 °C. Experimental results showed that both the high- and low-purity AAOs synthesized at 25 °C led to enhancements of the intensity of the PL peak by about 3.7–5.5-fold, depending on the Al purity and deconvoluted peak wavelength. These improvements were attributed to the high temperature enhancing the AAO thickness and reaction rate, thereby enabling more fluorescent ions to diffuse into the AAO for increased vacancy defects.

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## 1. Introduction

The anodization technique has long been used as an oxide layer to protect against corrosion on the surface of Al [1]. Anodic aluminum oxide (AAO) containing ordered pore channels can be used for improving the performance of solar cells [2], storage devices [3,4], sensors [5,6], self-cleaning surfaces [7], surface wetting [8] and so on. AAO can be prepared in a variety of electrolytes, including sulfuric acid, oxalic acid, or phosphoric acid, and has received much attention in recent decades. More specifically, since the blue light emission from AAO was discovered, the photoluminescence (PL) mechanism and application of AAO has been the focus of much research. Yamamoto et al. [9] studied the PL properties of AAO thin films formed in an oxalic acid electrolyte. Results showed a blue PL peak around 470 nm, which was attributed to the light-emitting property of oxalate ions diffused into the cell wall to form AAO luminescence centers under an electric field. Huang et al. [10] suggested that the light emission was from the defect states of the AAO film. In particular, they reported oxygen ions F<sup>+</sup> centers (oxygen vacancy trapping an electron i.e. singly charged oxygen vacancies) and F centers (oxygen vacancy trapping two electrons), which showed light-emitting peaks at 413 nm and 430 nm, respectively.

Khan et al. [11] attributed variations in the measurements of the PL peaks from AAO to different types of acids, such as oxalic acid, sulfuric acid or phosphoric acid. In brief, they found that the acid's ions and/or oxygen vacancies caused the AAO PL phenomenon. While numerous investigations have discussed the relationship between the PL peak and different kinds of electrolyte, fewer studies have considered the effects of aluminium (Al) purity and high electrolyte temperature.

In this article, the purity and temperature effects on the PL behavior of AAO due to both high (99.99%) and low (99%) purity Al are investigated. Compared with previous studies that have used traditional direct-current anodization at low temperature (0–10 °C) [11–13], we introduce a hybrid-pulse anodizing technology [14,15] to fabricate AAO at room temperature (25 °C). The higher temperature causes more fluorescent ions to diffuse into the AAO for enhancing the PL. The relationship between the PL phenomenon, Al purity and electrolyte temperature are then correlated according to the SEM plane-view image, cross section and PL spectra of AAO.

## 2. Experimental procedures

High- (99.99%) and low-purity (99%) Al foils (Alfa Aesar, USA) were used for one-step anodization under the same conditions for comparison. The impurities in the 99% Al primarily contained

\* Corresponding author.

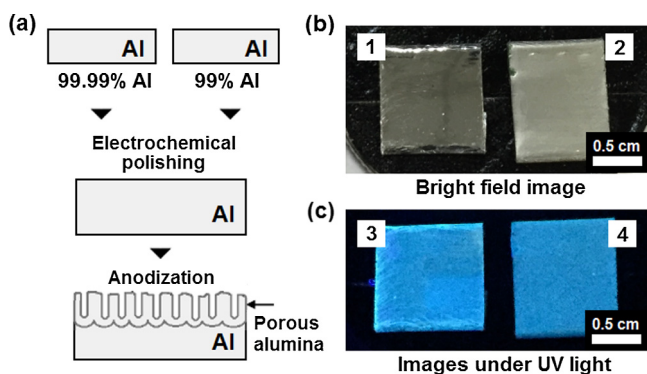
E-mail address: [ckchung@mail.ncku.edu.tw](mailto:ckchung@mail.ncku.edu.tw) (C.K. Chung).

a combination of Fe and Si, accounting for about 0.7%, while other impurities included Zn, Cu, Mg, Mn and Ti, together comprising about 0.3%. Before anodization, the Al foils were cleaned and electropolished in a mixture of  $\text{HClO}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  (volume ratio 1:2) at 20 V for 5 min. The single-step anodization of the Al thin films was performed in 0.3 M oxalic acid at 5 °C and 25 °C for 2 h by hybrid pulse technology to reduce the Joule heat. A hybrid pulse was constructed from a normal-positive square wave voltage (40 V) and a small-negative square wave voltage (−2 V), the hybrid-pulse period of which was 2 s (1 s: 1 s) [14,15]. It is noted that the anodizing current density during the negative potential duration is close to zero, which aids in the cooling and thermal relaxation to remove Joule's heat. The formation of AAO was performed via a potentiostat (Jiehan 5000, Taiwan) using a three-electrode electrochemical cell with platinum mesh as the counter electrode, the aluminum foil as the working electrode, and  $\text{Ag}/\text{AgCl}/3\text{ M KCl}$  as the reference electrode. The size of all specimens was  $1\text{ cm}^2$ .

After the anodization step, a comparison of the surface morphology and irradiated color of the AAO films was performed by High Resolution Field Emission Scanning Electron Microscopy (HR-FESEM, JEOL JSM-7001, Japan) and optical images. The luminescent color images were irradiated under 325 nm UV light at a distance of about 30 cm in a dark room, and taken by a camera also at a distance of about 30 cm but at an angle of about  $10^\circ$  from the UV light. The AAO element compositions were examined by Energy-dispersive X-ray spectroscopy attached to the HR-FESEM. The PL spectra of the AAO was excited by a 325 nm wavelength He-Cd laser in the PL spectrophotometer (Jobin Yvon Larbram/HR 800 Micro PL, France).

### 3. Results and discussion

Fig. 1a shows the schematic process flow of the one-step anodization of both the high- (99.99%) and low-purity (99%) Al foils at 40 V and 25 °C for 2 h. Fig. 1b shows the bright field image of the AAO films, in which label 1 represents the high-purity Al and label 2 the low-purity Al. The high-purity AAO had a “gloss like” surface while the low purity AAO had a matte surface. The impurities of Fe or Si, as listed in Table 1, in the low-purity Al induced an uneven distribution of the electric field during electropolishing and anodizing, which resulted in a coarse surface. Fig. 1c shows the optical images of the AAO samples in 1(b) irradiated under 325 nm UV light to induce the PL phenomenon. The images indicate that a bright blue emission occurs over the whole sample.



**Fig. 1.** (a) Schematic process flow of one-step anodization of both high- (99.99%) and low-purity (99%) Al foils; (b) the bright field images of AAO films which with label 1 from 99.99% Al and label 2 from 99% Al; (c) Optical images of 1(b)'s AAO samples (1 into 3, 2 into 4) irradiated under 325 nm UV light with a distance about 30 cm in a dark room. The anodization was performed at the same parameters of 40 V, 25 °C for 2 h.

**Table 1**

The mean weight percentage of element compositions of four kinds of AAO samples analyzed by EDS.

AAO sample	Al	O	Fe	Si
5 °C, 99% Al foil	44.1%	55.2%	0.5%	0.2%
5 °C, 99.99% Al foil	45.4%	54.6%	0	0
25 °C, 99% Al foil	44.1%	55.2%	0.5%	0.2%
25 °C, 99.99% Al foil	46.8%	53.2%	0	0

The high-purity AAO (label 3) has a higher PL brightness than the low-purity AAO (label 4), which may be attributed to surface topography or impurities. The PL intensity was further measured by Micro-PL spectroscopy excited by an He-Cd laser with a 325 nm wavelength.

Fig. 2a–e show the SEM plane-view images and cross sections of the AAO fabricated by one-step anodizing the 99.99% and 99% Al foils at 40 V and 25 °C for 2 h and the merged PL spectra, respectively. The images reveal that the pore configuration for both the 99.99% and 99% Al foils is in the short range order and that the AAO anodized from the 99.99% Al is slightly more regular than the 99% Al (Fig. 2a, b) with more measured Fe and Si impurity as listed in Table 1. The mean pore diameter for both the 99.99% and 99% Al foils was approximately 26.4 nm, while the respective thicknesses of the AAO (Fig. 2c, d) were measured to be 13.15 and 14.22  $\mu\text{m}$ , respectively. Both AAOs had a very high growth rate at 25 °C. The AAO from the low-purity Al had the higher growth rate of 7.11  $\mu\text{m}/\text{h}$  compared to the high-purity Al at 6.58  $\mu\text{m}/\text{h}$ . It was noted that the thicker AAO synthesized from the low-purity Al had a lower PL intensity than that of the high-purity Al, as shown in Fig. 2e. After deconvolution, the PL spectra of the high-purity AAO consisted of two bands, the peaks and intensities of which are 417 nm and 1636, and 480 nm and 1854, respectively. Moreover, the intensities of both bands were higher than those of the low-purity AAO, which consisted of 417 nm with a 1248 intensity and 480 nm with a 1560 intensity. In general, increasing the AAO film thickness tends to enhance its PL intensity. However, the reduced intensity of the thicker low-purity AAO could be due to the less regular or rough surface (Fig. 2b) scattering more light as well as the intrinsic impurities inhibiting the formation of luminescence centers of ions and oxygen vacancies.

AAO was also synthesized at 5 °C to understand the effect of electrolyte temperature on PL behavior. Fig. 3 shows the SEM plane-view images and cross sections of the AAO fabricated by one-step anodization of 99.99% and 99% Al foils at 40 V and 5 °C for 2 h as well as the merged PL spectra, respectively. The AAO formed at 5 °C exhibited a more disordered pore arrangement and smaller pore size (Fig. 3a, b) than that formed at 25 °C (Fig. 2a, b). The mean pore diameter at 5 °C was calculated to be about 18.0 nm; in other words, the porosity of the AAO at 5 °C was reduced to 9.8 compared to 17.3 at 25 °C. The measured thicknesses of the AAO at 5 °C from both the high- and low-purity Al foils (Fig. 3c, d) were 4.26  $\mu\text{m}$  and 3.53  $\mu\text{m}$ , respectively. The low-purity Al had a lower growth rate than the high-purity Al at low temperatures of 0–5 °C [12]. With respect to the temperature effect on AAO thickness, increasing the temperature to 25 °C apparently enhances the growth rate about 3–4 times compared to at 5 °C. This phenomenon of enhancing thickness and pore size of AAOs anodized in oxalic acid at the higher temperature of 25 °C can be explained by the Arrhenius formula (1).

$$\text{Rate} \propto e^{-Q/RT} \quad (1)$$

where *Rate* is the chemical reaction rate for the AAO thickness growth with the balanced oxidation and dissolution rate, *Q* is the activation energy of the chemical reaction, *R* is the gas constant, and *T* is the absolute temperature. Accordingly, increasing the tem-

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