Morphology and photoluminescence of nano-porous anodic alumina membranes obtained in oxalic acid at different anodization potentials

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Abstract
Porous Anodic alumina (PAA) with highly ordered pore geometry serves as an ideal template for future development of nanodevices. In the present work, PAA was prepared by varying anodization potential from 10 to 50 V in oxalic acid at 8 °C with a constant electrolyte concentration of 0.3 M. The influence of anodization potential on the structural and photoluminescence (PL) properties of PAA has been studied. The effect of anodization potential on the main pore characteristics of PAA such as pore diameter, interpore distance, pore density, porosity and circularity was studied. It was observed that circularity of PAA was nearly equal to one in the case of anodization potential of 40 V. Highest regularity ratio (RR) obtained for PAA formed in 40 V and it was calculated by WSX software. It was noticed that with increasing anodization potential there is a slight change in PL spectra of PAA and shows a strong PL peak in blue region.

1. Introduction

Nano-porous anodic alumina membranes were prepared using electro-chemical anodization method since the last two decades onward [1–3]. The formation mechanism of porous structure is still controversial [4], even though there is a lot of reports on applications of PAA in optical [5, 6], mechanical [7, 8] and structural [9–11] properties. Anodization to be derived by direct in situ methods is too difficult process [12], neither the scanning electron microscope nor the optical microscope can observe the process. The formation mechanism of PAA developed by several researchers, there is none of them provide correct data for the formation mechanism of entire anodization process [4]. Field-assisted dissolution theory [13, 14] cannot be clarified absolutely by Tong et al [15], even though the novel PAA nanostructures with well ordered pore arrangement was fabricated by that group. But formation mechanism of PAA based on voltage-time curves under constant current was explained recently using three-step anodization method by Zhang Kun et al [16].

It is well known that, after anodization in different electrolytes, there are two types of oxide films existing in PAA, namely the porous and compact oxide films. Some group of researchers already studied and published the difference between compact and porous alumina membranes [17, 18]. The best of our knowledge, the porous and compact alumina is formed by the anodization of aluminium in acidic solutions like H2SO4, H2C2O4 and H3PO4 [19–21] and in neutral solutions (boric, decanedioic, hexanedioic acid, etc) [22, 23]. The effect of anodization process parameters such as anodization duration, temperature [24] and electrolyte composition [25] on the pore mechanism of PAA already studied. The main pore parameters of PAA such as pore diameter, interpore distance and porosity depends on the anodizing conditions like nature of the electrolyte concentration, anodization potential, duration and temperature [11]. There are few studies reporting the relationship between the regularity ratio and anodization process parameters [26, 27].

The aim of this paper is to investigate the morphological and PL features of PAA by varying the anodization potential from 10 to 50 V. In the present work, the effect of anodization potential on pore characteristics such as
pore diameter, interpore distance and circularity were investigated, which could improves the understanding mechanism of anodization in PAA. Additionally, the PL analysis of PAA obtained in oxalic acid at various anodization potentials was discussed. The variation of RR with PL intensity by varying anodization potential was also discussed.

2. Experimental

PAA was prepared via two-step anodization of high purity aluminum foil (0.30 mm thickness) purchased from Alfa Aesar (99.999% Puratronic). Initially, Al foils were cut into coupons 20 × 20 mm [28], degreased in acetone and then electrochemically polished in solution having HClO₄ and C₂H₆O (1:4 in volume) at 15 V [29].

Anodizations were carried out with a constant electrolyte concentration of 0.3 M, duration of 12 h, at different anodization potentials from 10 to 50 V with a step of 10 V at 8 °C. For each anodization process distance between electrodes (4 cm) and a working area of the sample (1 cm) were kept constant. The formed alumina layer on the sample was removed in a mixture of 6 wt% H₃PO₄ and 1.8 wt% H₂CrO₄ at 60 °C for 2 h [30]. To obtain highly ordered porous alumina, second step anodization was carried out using the same anodic conditions for 12 h.

Surface characterizations of fabricated PAA were carried out using scanning electron microscope (JEOL/ JSM-6380LA). Image-J 1.5 and WSxM 5.70 softwares were used to study the quantitative assessment of the hexagonal arrangement of nanopores in PAA [31]. The PL Spectra were taken with Floromax-4 fluorescence spectrometer with a Xe lamp at room temperature using an excitation wavelength of 320 nm.

3. Results and discussion

To study the effect of anodization potential on structural aspects of PAA, anodization was performed at different anodization potentials from 10 to 50 V with a step of 10 V with a constant electrolyte concentration of 0.3 M at a temperature of 8 °C. Figure 1, shows the SEM micrographs (figures 1(a), (e), (i), (m), (q)), cross-sectional images (figures 1(b), (l), (j), (n), (r)), 2D Fast Fourier Transforms (FFT) images (figures 1(c), (g), (k), (o), (s)) and corresponding average profiles (figures 1(d), (h), (l), (p), (t)) of the FFT radius of PAA templates obtained by varying the anodization potential from 10 to 50 V. Reports on the pore arrangement discovered that the cell uniformity of PAA increases with anodization potential, from 10–30 V pore arrangement is not uniform and cell structure also not in hexagonal shape. When anodization was conducted at 40–50 V, uniform ordering of the pores increased intensely and cell structure was hexagonal in shape. FFT analysis revealed that, the highly ordered periodicity of the pores were observed in the case of 40–50 V because the FFT spectrum was in a ring shape. FFT Spectrum obtained in 20 and 30 V is disordered ring because of the low periodicity in pore arrangement, but in the case of 10 V disc shape spectrum was observed results reveal that pores are formed but not in uniform order. This attributes to increasing anodization potential leads to increase self-ordering of the pores and oxide layer thickness [27]. These observations are in good agreement with the result form figure 1. In case of anodization potential, the better array of pores obtained for PAA membranes prepared at 40 V (figure 1(m)). In other potentials (10, 20, 30, and 50 V), a decrease of regularity of the pores was observed. To evaluate the effect of anodization potential on morphology of PAA, anodization (both first and second steps) was done with DC anodization potentials from 10 to 50 V at constant anodizing duration of 12 h. The main pore characteristics such as pore diameter, interpore distance, pore density, porosity were calculated using the formulae reported in the publication [32, 33]. Porosity (α) of the PAA membranes calculated after obtaining the data of pore diameter (Dₚ) and interpore distance (Dᵢ) from image-J, using the formula:

\[ \alpha = \frac{\pi}{2 \sqrt{3}} \left( \frac{D_p}{D_i} \right)^3 = 0.907 \left( \frac{D_p}{D_i} \right)^3 \]  

(1)

The effect of anodization potential on pore diameter and interpore distance was shown in the figure 2. It was observed that, with increasing anodization potential from 10 to 50 V, pore diameter increase from 15 to 70 nm (figure 2(a)) and interpore distance also increases from 46 to 146 nm (figure 2(b)). From figure 2 results shows that, pore intervals (pore diameter and interpore distance) of PAA were greatly dependence on the applied potentials, showing a linear relationship to the applied anodizing potential [34]. A random arrangement of pores and a lack of uniformity of the pore shape were observed in PAA formed in 10, 20, 30 and 50 V. This fact was observed qualitatively from figure 1, by wide ring-shapes in FFT images. Circularity coefficient (C) is used to calculate the deviation of the pores shape from an ideal circle. If C = 1, indicates the pores shape is ideally circle, while C = 0.0 indicates the presence of deformed irregular shape of pores [35]. The circularity of the pores varies with anodizing potentials was shown in the figure 3. Circularity of the pores increases with increasing anodization potential form 10 to 40 V, then decreases for 50 V. A strong liner relationship between circularity of the pores and PAA formed at different anodization potentials was observed and circularity nearly equal to one.
Pore characteristics (pore diameter, interpore distance, porosity and pore density) data of PAA were tabulated in Table 1. In order to study the in depth analysis of regularity of the pores, regularity ratio (RR) of the pores was calculated from the FFT images for all anodizing potentials. The dependence between RR and anodization potentials was shown in the figure 4.

RR of the pores increases linearly for PAA formed in 10–40 V [36] and decreases for 50 V. RR of PAA formed in 40 V is very high value, this is due to highly ordered uniformity of the pores were observed in PAA formed in 40 V. Photoluminescence (PL) spectra of PAA estimated at 10, 20, 30, 40 and 50 V were shown in figure 5. PL emission spectra were observed in all PAA in the blue region (300–600 nm) with an excitation wavelength of 320 nm [37]. It was noticed that with

Table 1. Pore characteristics data of PAA formed in different anodization potentials.

| Anodization potential (V) | Pore diameter (nm) | Interpore distance (nm) | Circularity (%) | Porosity (%) | Pore Density (10 x 10 cm⁻²) |
|--------------------------|--------------------|------------------------|----------------|--------------|-----------------------------|
| 10                       | 15                 | 46.2                   | 0.74           | 51.6         | 0.024                       |
| 20                       | 30                 | 68.7                   | 0.82           | 59.9         | 0.054                       |
| 30                       | 42                 | 91.7                   | 0.91           | 61.3         | 0.097                       |
| 40                       | 61                 | 128.3                  | 0.99           | 62.5         | 0.19                        |
| 50                       | 69                 | 146.4                  | 0.92           | 62.2         | 0.24                        |

(∼0.99) in the case of PAA formed in 40 V.
Figure 2. Effect of anodization potential on pore intervals of PAA: (a) Pore diameter and (b) Interpore distance.

Figure 3. Circularity of PAA as a function of anodization potentials.

Figure 4. Regularity ratio of PAA as a function of anodization potentials.
increasing anodization potential leads to a slight shift in the emission peaks towards the visible range. It should be noted that shift rate is more from 10–30 V, and it decreases afterwards (40–50 V). It could be deduced that in these membranes, with increasing anodization potential (~30 V) improves formation of optically active defects, which are in the visible range. The Gaussian fitting analysis of all these membranes were shown in the figures 5(b)–(f). The maximum emission peak varies with anodization potential and maximum peak observed at 465 nm for 50 V, which is middle of the blue region. PL activity of PAA in the visible region improves this wavelength shift [38]. Therefore, it could be inferred that with increasing anodization potential beyond 40 V has insignificant shifting effect on the emission spectrum (figure 5(f)). These findings show that PL activity of the PAA in the visible range cannot improves with increases the anodizing voltage beyond 40 V. The PL intensity of F centers varies with anodization potential (10–417, 20–415, 30–415, 40–420 and 50–417 nm) which are in violet region, where as F+ centers of 10, 20, 30, 40 and 50 V are 420, 457, 455, 467 and 465 nm which are in blue region. In table 2 all the values of PL spectra (F and F+ centers) of PAA and RR were tabulated. The shift of PL peak position varies with anodization potential, maximum for 50 V (48 nm) and minimum for 10 V (3 nm) between

Figure 5. PL spectra (a) and Gaussian fitting analysis of PAA membranes obtained at different anodization potential (b) 10, (c) 20, (d) 30, (e) 40 and (f) 50 V in 0.3 M of oxalic acid.
two centers was shown in the figure 5. With increasing anodization voltage up to 40 V, widens the sub bands width, and beyond 40 V, no sensible effect was observed. These investigations may be useful for explaining the pore formation mechanism of AAM and structural tuning ability to control over the PL properties of alumina membranes.

4. Conclusions

PAA was successfully obtained through two-step anodization in oxalic acid at various anodization potentials from 10 to 50 V with a step of 10 V. Effect of anodization potential on pore characteristics (pore diameter, interpore distance, porosity and pore density) were studied. Pore diameter and interpore distance varies linearly with anodization potential were observed. Circularity and regularity ratio of pores depends on anodization potential was investigated and highest regularity ratio and circularity of the pores were observed in 40 V PAA. Further, the PL measurements of PAA were investigated at different anodization potentials. It was found that PL spectra show an asymmetrical pattern in blue region and spectrum was divided into two sub-bands (F and F^+ centers) by Gaussian analysis. PL intensity increases with increasing anodization potential and maximum for PAA obtained in 50 V.

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**Table 2.** Regularity ratio and PL data of PAA obtained in different anodization potentials.

| Anodization potential (V) | Regularity ratio (a.u.) | F^+(λ₁) (nm) | F(λ₂) (nm) | PL Intensity (a.u.) |
|--------------------------|-------------------------|-------------|------------|---------------------|
| 10                       | 1.57                    | 420         | 417        | 391347.8            |
| 20                       | 1.79                    | 457         | 415        | 557972.5            |
| 30                       | 2.43                    | 455         | 415        | 600287.6            |
| 40                       | 5.77                    | 467         | 420        | 1110000             |
| 50                       | 3.68                    | 465         | 417        | 1320000             |
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