

## Research Article

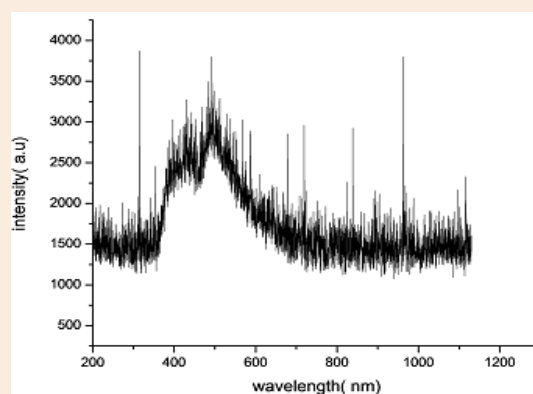
## Fabrication of Porous Anodic Alumina by Two Step Anodic Oxidation and Photo Luminescent Properties of Doped and Undoped Alumina

Naveen Verma\*<sup>1</sup>, Krishan Chander Singh<sup>1</sup>, Bernabe Mari<sup>2</sup>, Hari Om<sup>1</sup>, Jitender Jindal<sup>1</sup><sup>1</sup>Department of Chemistry, Maharshi Dayanand University, Rohtak-124 001, India<sup>2</sup>Departament de Física Aplicada, Universitat Politècnica de València, 46022 València, Spain.**Abstract**

Porous anodic alumina was prepared by two step anodic oxidation process which is much less expensive method than other methods like lithography, optical diffraction grating etc to achieve symmetrical pores. The first step of anodization was carried out in 0.3 M oxalic acid at 40 V. In the second step, the anodization was done at constant current density of 5mA/cm<sup>2</sup> for 1 hour in 0.3 M H<sub>3</sub>PO<sub>4</sub>. Both the anodization steps were carried out at 15°C temperature. The second step anodic oxidation in H<sub>3</sub>PO<sub>4</sub> produced very symmetrical pores. The morphology of porous oxide film was studied by FESEM. The porous anodic alumina was doped with Eu<sup>3+</sup>. The photoluminescence of doped and undoped alumina oxide was studied. The photoluminescence property in PAA membrane is attributed to the presence of F and F<sup>+</sup> centres.

**Keywords:** Porous anodic alumina, Photoluminescence, Anodization

Doped porous anodic alumina gives a very high intensity luminescent peak near 600 nm (red region) due to Eu<sup>3+</sup>.

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**Introduction**

The anodic oxide film on aluminium structurally can be classified in two types – barrier type and porous type. The barrier type thin films are very compact and used in protection and capacitor technology [1-3]. Porous anodic oxide film on aluminium acts as a good template for growing nanomaterials [4-6]. Nanomaterials has attracted attention due to their unique properties and highly characteristic application in electronic, optic and another magnetic storage device [7-8]. The attention has been paid to search the methods which are time saving and nonexpensive for the fabrication of nano materials. Template assisted synthesis of nanomaterials are now widely used [9]. The porous anodic alumina template may be used as nanofilters due to nanosize pore diameter. The nanotemplates of porous anodic alumina are also widely used as template for the formation of nanomaterials of semiconductors like Si, Ge, GaN, CdS, ZnO. For the use of porous anodic alumina as a template some controlled morphology should be obtained. For the formation of controlled morphology of porous structure, a two step oxidation method is widely used [10-11]. The method involves the washing of anodic oxide film formed in first step and then anodized again at the same or different conditions. The washed templates after first anodization provide imprintation for the growth of pores in second step. The typical electrolytes in which anodization works were carried out are sulphuric, oxalic and phosphoric acid. Anodization in different acids produces different pore size. Higher pore diameter was obtained by anodization of aluminium in phosphoric acid but the pores are not symmetrical as obtained in oxalic acid. During anodization of aluminium in sulphuric acid and phosphoric acid there is burning effect and less symmetrical porous structure were obtained as compare to oxalic acid. Aluminium anodization in phosphoric acid produces porous structure in a wide range of voltage (60 to 190V) but voltage above 150V, well order pore array can be obtained. The higher voltages

used during anodization causes the problem of burning which cause more dissolution of the oxide film. When higher anodization voltages are applied during second anodization more than one pore per cell may grow. The problem of anodization in phosphoric acid may be decreased by standardization of conditions of anodization like temperature, concentration or use of some additives in the electrolyte. The first approach towards this is the lowering of temperature of electrolyte during anodization which reduced the burning effect. The second approach towards this is to use alcohol as an additive which decreases the temperature of electrolyte significantly and also reduces the joule heating effect at the pore bottoms. The cooling effect on addition of alcohol is due to the evaporation of low freezing alcohols at aluminium/oxide interface which effect the pre rearrangement time [12].

In this study we have fabricated symmetric porous hexagonal cells for the anodization in phosphoric acid at current density of  $5\text{mA}/\text{cm}^2$ . The first step of anodization was done in  $0.3\text{M}$  oxalic acid at  $40\text{V}$  for 1 hour. Due to first anodic oxidation in oxalic acid, symmetrical pores were obtained in finally formed porous anodic alumina in phosphoric acid.

Beside the use of porous oxide as nanotemplate,  $\text{Al}_2\text{O}_3$  may be used as host lattice for different inorganic ions. The porous alumina embedded with xerogel doped with lanthanide ions has been reported [13]. For the formation of these films, CVD, spray pyrolysis type techniques were widely used but these are expensive.

This work involves the preparation of porous anodic alumina template (as discussed above) doped with  $\text{Eu}^{+3}$  ion just by boiling the porous alumina in simple  $\text{Eu}(\text{NO}_3)_3$  solution for just 30 minutes and further annealing of separated alumina film at  $800^\circ\text{C}$  for 1 hour. The luminescence characteristic has been studied.

## Experimental Procedure

A high purity aluminium foil (99.997%, Alfa Aesar) was used as starting material. First of all aluminium substrates were mechanically polished with fine grade silicon carbide paper followed by chemical etching with  $\text{NaOH}$  ( $100\text{ gm}/\text{litre}$ ). Then the samples were electro polished in a mixture of  $\text{HClO}_4:\text{C}_2\text{H}_5\text{OH}$  (1:5) for 3 minute at constant voltage of  $15\text{ V}$ . After electro polishing the samples were successively rinsed with distilled water, ethanol and dried. The samples were anodized by two step procedure for the fabrication of alumina film. In the first step the samples were anodized in  $0.3\text{ M}$  oxalic acid for 1 hour at a constant voltage of  $40\text{ V}$ . The prepared alumina layer was washed with an etching mixture of  $6\text{ wt}\%$   $\text{H}_3\text{PO}_4$  and  $1.8\text{ wt}\%$   $\text{H}_2\text{Cr}_2\text{O}_4$  at  $60^\circ\text{C}$  for 2 hours. Then the second anodization was performed for 1h in  $0.3\text{M}$  phosphoric acid at a constant current density of  $5\text{mA cm}^{-2}$ . Anodization was performed in a simple electrochemical cell with magnetic stirrer under the constant temperature of  $15^\circ\text{C}$ . The working surface of sample was  $1\text{cm}^2$ . A Platinum mesh was used as cathode. The samples were placed in centre of the platinum mesh. The porous anodic template is separated from aluminium by dipping in  $\text{HgCl}_2+\text{HCl}$  solution. Before this, nail polish is applied to support the thin brittle film. The nail polish coating is then washed in acetone to obtain porous anodic alumina template. The study involves the formation and morphological characteristic and luminescent properties of doped and undoped porous alumina formed in  $\text{H}_3\text{PO}_4$ .

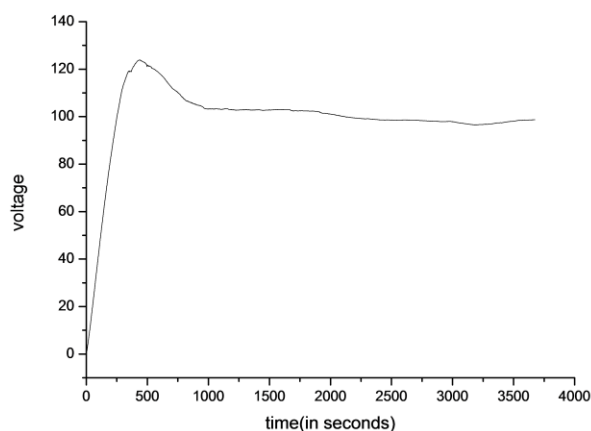
The surface morphology of the film was investigated by FESEM. The crystallography structure of porous alumina was analyzed by means of high resolution XRD using Rigaku ultima IV diffract meter in the  $\theta-\theta-2\theta-\theta$  configuration and using  $\text{Cu K}\alpha$  radiation ( $1.54184\text{\AA}$ ).

## Result and discussion

### Voltage Time Characteristics

The voltage time curve for anodization in  $\text{H}_3\text{PO}_4$  is shown in **Figure 1**. In the first part of curve the voltage increase linearly up to 400 second shows a peak and there is small drop in voltage followed by a constant value of voltage up to the end of anodization. This curve involves three stages; first linear increase in voltage with time is attributed due

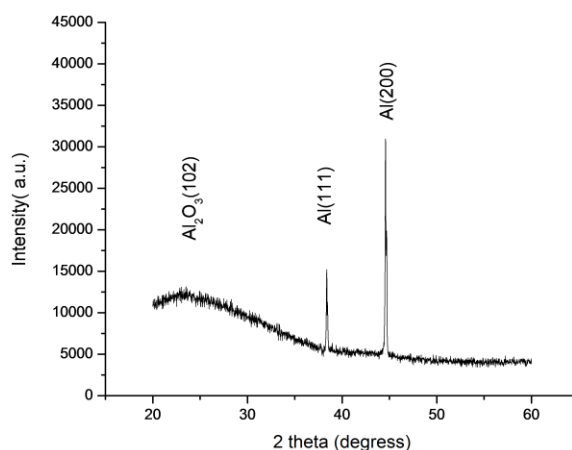
to the formation of barrier oxide film on aluminium surface. Due to field assisted dissolution and formation of pores in alumina leads to decrease in voltage in the 2<sup>nd</sup> part. After drooping voltage there is steady state voltage due to equilibrium in field assisted dissolution of alumina membrane and simultaneous formation of oxide film at the metal oxide interface [14].



**Figure 1** Voltage- time curve for anodizing of aluminium in phosphoric acid at a constant current density of  $5 \text{ mA cm}^{-2}$

### XRD Measurements:

The intact  $\text{Al}_2\text{O}_3$ , not separated from aluminium substrate without annealing is subjected to XRD. The diffraction pattern shows the amorphous nature of alumina along with peaks corresponding to aluminium (**Figure 2**). The observations are agreement with reference [15].



**Figure 2** XRD pattern of anodic alumina intact with aluminium

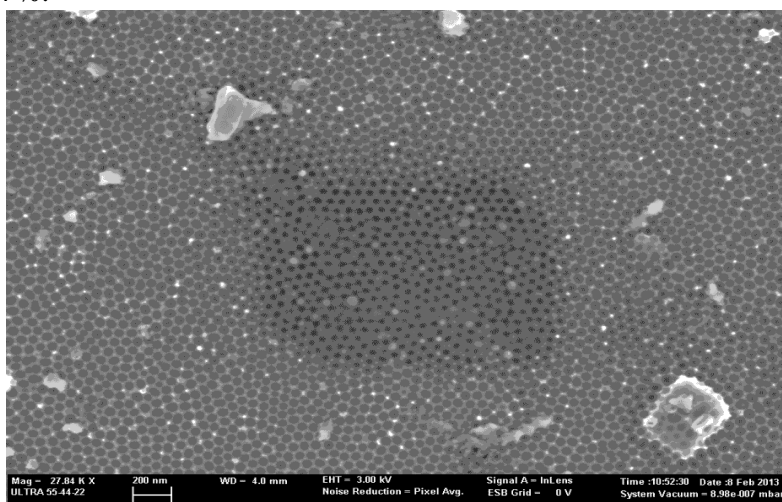
### Surface Morphology

It is difficult to obtain very symmetrical porous structure of alumina in  $\text{H}_3\text{PO}_4$  anodization. The anodization in phosphoric acid produced homogenous porous structure only at higher voltage (150V). According to the reported work [16] mechanical structure metal/oxide interface forces the alumina cells to form hexagonal pore bottom arrays. In  $\text{H}_3\text{PO}_4$  anodization small currents were observed during the pore nucleation and formation which leads to lower

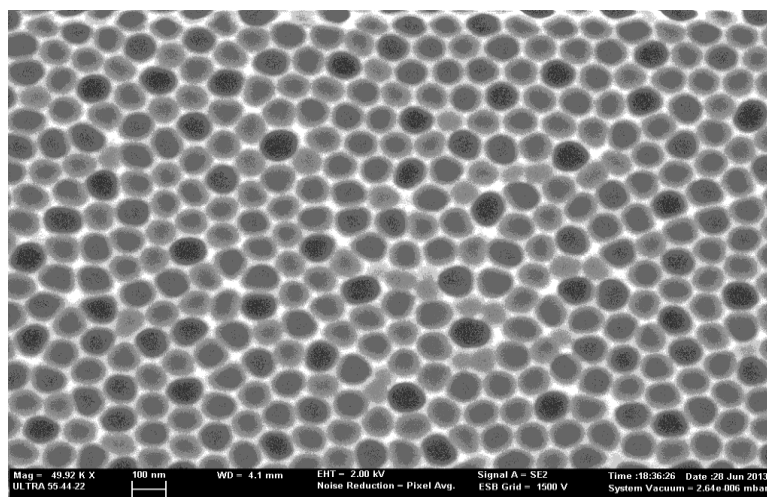
mechanical stress at metal oxide interface which is not enough to regulate the bottom pore arrays to grow in order manner. In our work the aluminium first anodized in oxalic acid (0.3M) at 40V and then oxide film was dissolved in 6wt%  $\text{H}_3\text{PO}_4$  and 1.8wt%  $\text{H}_2\text{Cr}_2\text{O}_4$  showed concave patterned surface (**Figure 3**). The produced concavities provide excellent pretexture for the growth of symmetrical hexagonal porous alumina. The pretexturing by oxalic acid anodization enhances the chances of achieving order pore array despite of above weak mechanical forces. It means first anodization highly guided the growth of pores in IInd anodization. The morphologies of anodic alumina sample measured with FESEM (**Figure 4**). Morphological parameters such as pore diameter, interpore distance, and pore density were obtained by image analysis from FESEM picture. Porosity was obtained by following ratio,

$$\text{Porosity \%} = (S_{\text{pore}}/S_{\text{oxide}}) \times 100$$

Where,  $S_{\text{pore}}$  is the total surface area of pores and  $S_{\text{oxide}}$  is the oxide geometric surface. The average pore diameter and average interpore distance was found 94 nm and 120 nm respectively. The calculated porosity according to formula as discussed above is 69.14 %.



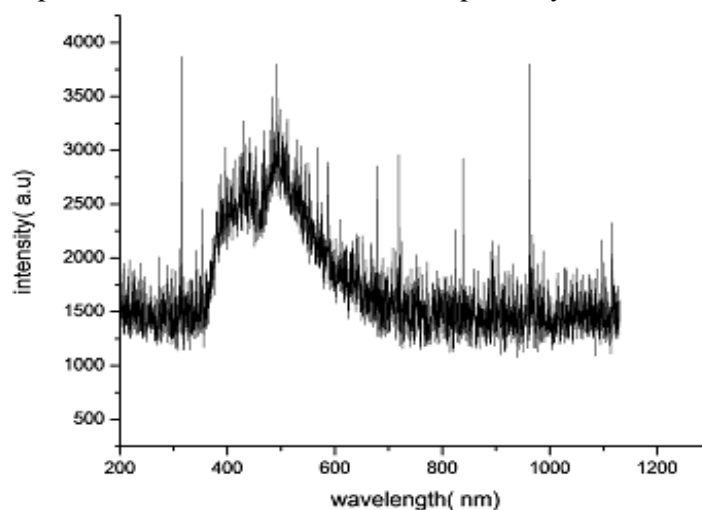
**Figure 3** Concavities in the film formed after anodization at 40 volt preceded in 0.3 M oxalic acid at 15°C and washed in mixture of 6wt%  $\text{H}_3\text{PO}_4$  and 1.8wt%  $\text{H}_2\text{Cr}_2\text{O}_4$  at 60°C for 3 hours



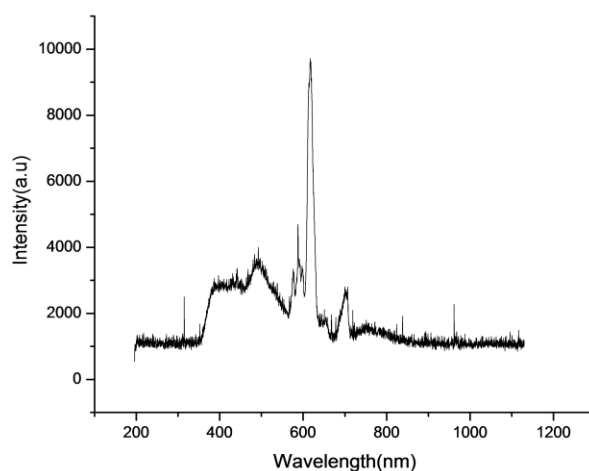
**Figure 4** FE-SEM images of aluminium after final anodization in 0.3 M phosphoric acid at a constant current of  $5\text{mA}/\text{cm}^2$

### Photoluminescence properties

Photoluminescent spectra of formed anodic oxide film in  $\text{H}_3\text{PO}_4$  were in **Figure 5**. The spectra show a peak at 432 nm and 490 nm wavelength. In anodization, there are two opposite process – film formation and film dissolution. Oxygen ion transfers in the electrolyte and migrate through the barrier layer under a high electric field [ $10^6$ - $10^8$ V/cm] by a vacancy mechanism [17]. This indicates that many oxygen ions exist in anodic alumina. The F centres were produced due to partial oxygen vacancies. The presence of these oxygen vacancies are considered for giving photoluminescence properties. The luminescent centres exist in both pore walls and barrier layer of anodic oxide film. The electrolyte has large influence in the light emitting property of alumina membrane. In phosphoric acid at intensity band at 432 nm and 490 nm is attributed to the presence of  $\text{F}^+$  and F and centre respectively in anodic alumina.



**Figure 5** Photoluminescence spectra of anodic oxide film formed in phosphoric acid



**Figure 6** Photoluminescence spectra of anodic oxide film after boiling in  $\text{Eu}(\text{NO}_3)_3$  solution and annealing

**Figure 6** shows the luminescent spectra of alumina sample separated from alumina and doped with  $\text{Eu}^{+3}$  ions and annealed at  $800^\circ\text{C}$  for 1 hour. The photoluminescent spectra shows a broad peak at 491 nm (due to F centre) and sharp peak at 588 nm, 615 nm and 703 nm corresponds to  $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  &  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transition due to europium ions. The intensity of the peak clearly indicates that the luminescence is due to rare earth photo luminescent. It is believed that  $\text{Eu}^{+3}$  ions from aqueous  $\text{Eu}(\text{NO}_3)_3$  solutions were adsorbed by the amorphous alumina and then  $\text{Eu}^{+3}$  incorporated in alumina due to process of annealing.

## Conclusion

Porous anodic oxide film incorporated with  $\text{Eu}^{+3}$  ions may be used as light emitting material. High intensity photo luminescent were observed from porous anodic alumina template sealed in  $\text{Eu}(\text{NO}_3)_3$  solutions and annealed at  $800^\circ\text{C}$  for 1 hour. Anodic oxidation in oxalic acid in the first step imparts imprintation for the growth in  $\text{H}_3\text{PO}_4$  in second step in which the produced highly symmetrical porous structure. Photo luminescence in the anodic oxide film proposed to originate from recombination centered related to oxygen defects formed during aluminium oxidation.

## Acknowledgements

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