Structure dependent photoluminescence of nanoporous amorphous anodic aluminium oxide membranes: Role of F\(^{+}\) center defects

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ABSTRACT

The origin of photoluminescence (PL) of the anodic aluminium oxide (AAO) membranes synthesized by electrochemical anodization of aluminium by using oxalic, phosphoric and sulfuric acid electrolytes for different anodization time duration have been investigated. All the as prepared AAO membranes exhibit strong visible blue luminescence around 410–430 nm at room temperature. The mechanism of the visible light emission in AAOs has been explained by correlating the structural studies of the membranes with the PL and electron paramagnetic resonance (EPR) spectroscopy measurements. It is found that the AAO membranes are amorphous in nature (XRD and HRTEM study) and they contain large concentration of structural of defects (HRTEM study). The extensive PL and EPR investigations have indicated the presence of singly ionized oxygen vacancy related defects (F\(^{+}\) center defects) in AAO membranes. Based on the experimental evidences, the F\(^{+}\) center defects are attributed to the visible blue light emission from the AAOs.

1. Introduction

Self-organized nanoporous anodic aluminium oxide (AAO) membranes synthesized by controlled electrochemical anodization of pure aluminium in acidic medium [1–2] have been employed extensively as the host for 1D nanostructures like nanowires, nanorods and nanotube of different metals, semiconductors and polymers [3–7] because of its uniform structure and stability. AAO membranes containing ordered cylindrical pores of nanometer scale diameter inside the honeycomb like arrays have been studied for a long time [1,8]. Recently, photonic crystal behavior [9] and optical properties [10–12] of AAO membranes have been examined. Investigation of the optical properties of AAO membranes itself is very important as it has significant influence on the optical properties of the materials grown within its pores. Moreover, the study of the optical properties of AAO membrane is also crucial from the viewpoint of their technological applications as light emitting devices [13], photonic material [14] and laser devices [15]. It is found that the AAO membranes exhibit strong luminescence characteristics when exposed to ultraviolet light. For the first time, Du et al. [16] have reported that the AAO films prepared by using oxalic acid electrolyte exhibit photoluminescence (PL) in the blue wavelength region.

However, till date many works have been focused to investigate the origin of the inherent PL of AAO membranes. Gao et al. [17] have demonstrated that the light emission from AAO membranes prepared in 0.3 M oxalic acid solution is due to PL centers originated from the oxalic impurities incorporated into the porous oxide layer during anodization. The transformed carboxylic impurities related luminescence centers were found to be responsible for the PL from the AAO films grown by high field anodization process [11]. Very recently, Li et al. [18] also have reported that the luminescent centers originated from sulfuric and oxalic impurities are responsible for the luminescence characteristics of AAO membranes prepared using a mixture of oxalic and sulfuric acid electrolyte. Furthermore, the presence of oxygen vacancy related defect centers has also been attributed to the origin of visible PL in the AAO by different researchers [16,19–21]. However, to date, the mechanism behind the light emission of the AAO membranes remains very ambiguous, complicated, and bewildering. Hence, more in-depth studies on the luminescence characteristics of the AAOs are essential to reveal the origin of the photo emission characteristics.

In this report, we describe the PL property of the as prepared AAO membranes fabricated in oxalic, phosphoric and sulfuric acid electrolytes. The luminescence mechanism of the AAO membranes has been explained correlating the results of the PL and electron paramagnetic resonance (EPR) spectroscopy measurements with the information of their structural properties obtained from the x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The studies indicate that the oxygen deficiency related structural defects are responsible for the light emission from
the AAO membranes. The morphology of the AAO membranes has been investigated by scanning electron microscopy (SEM).

2. Experimental methods

AAO membranes were synthesized by the conventional two-step anodization of high purity (99.99%) aluminium foils [1, 22]. The aluminium foils were annealed at 400 °C for 4 h for the necessary grain enlargement and then electropolished at 40 V for 20 s using the acidic electrolyte solution of 75 ml HClO₄, 730 ml methanol, 95 ml butyl cellosolve and 100 ml distilled water employing an automatic electrolytic polishing setup (Electropol-II, Metatech Industries, India). The electropolished samples were degreased in acetone and kept in an ultrasonic vibration bath for cleaning. The two-step electrochemical anodization of the aluminium foils was carried out separately in 3 wt% oxalic, sulfuric and phosphoric acid electrolyte solution to fabricate AAO membranes. AAO membranes were prepared in oxalic acid solution by varying the D.C. anodization voltage in between 50 and 55 V maintaining a constant current density of 200 A/m². For the AAO membranes synthesized using phosphoric and sulfuric acid electrolytes, D.C. anodization voltages were controlled between 40–45 and 25–30 V, respectively to maintain a constant current density of 200 A/m². The first-stage anodization was carried out for 30 min at 10 °C for all the cases. The nanoporous alumina layer grown on the surface of aluminium foil after the first-stage of anodization was removed by chemical etching using a mixture of 60 wt% phosphoric, 28 wt% H₂SO₄ and 12 wt % HNO₃ acid solution and the foils were re-anodized for the second time keeping all the anodization parameters the same as those in the first-stage to obtain more uniform porous structure. All the membranes were cleaned several times in double distilled de-ionized water to remove the acidic inclusions from them. AAO membranes prepared in oxalic, phosphoric and sulfuric acid electrolytes for 2, 4 and 6 h of second stage anodization are denoted as AO2, AO4 and AO6; AP2, AP4 and AP6; AS2, AS4 and AS6, respectively.

The morphology of the as prepared AAO membranes was examined by scanning electron microscopy (SEM, Hitachi S-3400N). The crystallographic nature of the membranes were studied by using x-ray diffractometer (XRD, Philips Panalytical PW 1830 diffractometer) with Co Kα (λ=1.78901 Å). The elemental composition of the membranes was analyzed by energy dispersive x-ray (EDAX) attached with SEM. TEM and high resolution TEM (HRTEM, JEOL, JEM-2100) were used to obtain more information about the crystalline structure of the membranes. For the TEM study the AAO membranes grown on the surface of the aluminium foil were separated from the substrate by applying a reverse voltage of 50 V for 5–10 min inside the electrochemical bath. The room temperature PL characteristics of the AAO membranes were recorded by using a spectrofluorometer (Horiba Jobin Yvon, Fluorolog-3) having a Xe lamp as the light source under the excitation of the 315 nm light. The membranes were examined by EPR spectroscopy (Jeol JES-FA100) in order to get an idea about the structural defects present in AAOs.

3. Results and discussion

3.1. Morphological and structural characterization

3.1.1. SEM and EDAX studies

Fig. 1(a), (b) and (c) shows the representative SEM micrographs of the as prepared porous top surface of the AAO membranes fabricated by using oxalic, phosphoric and sulfuric acid electrolyte solution after 6 h of second stage anodization, respectively. It is evident from Fig. 1(a) that the average size of the pores of the AAO membrane prepared using oxalic acid solution is about 45–50 nm. Whereas the average size of the pores of the AAO membrane prepared by using phosphoric and sulfuric acid solutions is in the range of 100–120 and 100–130 nm, respectively. The inset of Fig. 1(a) shows the SEM image of the AO6 after the pore opening treatment, in which the membrane is dipped in 10 wt% phosphoric acid solution for 30 min. Homogeneous distribution of the nanopores

![Fig. 1. SEM micrographs of the as prepared AAO membranes: (a) AO6 (inset: AO6 after the pore opening treatment), (b) AP6 and (c) AS6 and the corresponding (d) EDS spectra.](image-url)
of uniform diameter is evident from the figure (inset Fig. 1a). The studies on the cross-section of AAOs indicate that the thickness of the membranes increases with the increase of the anodization time. Fig. 1(d) shows the EDAX spectra of the AAO membranes fabricated using oxalic, phosphoric and sulfuric acid electrolyte solutions. The elemental analysis indicates that the AAO membranes contain Al and O only, whereas the presence of the little amount of C, P and S appear because of the acidic inclusions from the electrolyte solution.

3.1.2. XRD study
Fig. 2 shows the representative XRD patterns of the as-prepared thick porous AAO membranes synthesized by using oxalic, phosphoric and sulfuric acid electrolyte after 6 h of second stage anodization. Here, it is worthwhile to mention that all the AAO membranes fabricated in different electrolyte solution for different anodization times provide a similar response under XRD measurements. In the XRD pattern (Fig. 2) no sharp diffraction peaks are observed from any particular crystallographic plane of the porous AAO membranes. Hence, it can be inferred that the AAO membranes are noncrystalline in nature.

3.1.3. TEM study
The detailed information about the structure and crystallographic nature of the AAO membranes can be obtained by TEM and selective area electron diffraction (SAED) pattern characterization. Fig. 3(a) shows the representative TEM image of the AAO membrane containing the nanopores fabricated using oxalic acid electrolyte. The dark spots in the TEM images represent the pores of the AAO membrane and the bright region corresponds to the alumina layer in between the pores. It is evident (Fig. 3(a)) that the average pore size is in the range of 40–50 nm. Fig. 3(b) shows the HRTEM micrograph of the alumina layer (from the marked region of Fig. 1(a)) of the AAO membrane with the corresponding SAED pattern in the inset. The amorphous nature of the AAO membrane is evident from Fig. 3(b), where the as grown alumina layer has no specific lattice order and the atoms are oriented in a random fashion. The HRTEM studies on the AAO membranes vividly indicate the presence of large concentration of structural defects in the noncrystalline membranes. Furthermore, the diffused SAED pattern of the AAO (inset of Fig. 3(b)) clearly indicates the amorphous nature of the AAO membrane. It is found that all the AAO membranes grown on aluminium substrate by using different electrolyte solutions are amorphous in nature and they contain large concentrations of structural defects.

3.2. Defect formation mechanism in AAOs
The mechanism of the incorporation of structural defects in AAO membranes could be understood by examining the synthesis process of the membranes carefully. During the growth of the AAO membrane on aluminium substrate through electrochemical anodization, compressive stresses of large magnitude is generated at the aluminium/alumina interface due to the volume expansion caused by the conversion of aluminium to alumina [23]. Moreover, the anodization of aluminium is an exothermic electrochemical reaction, which also generates thermal energy during the growth of the AAO membrane in Al foil substrate. Therefore, the interfacial compressive stress coupled with the thermal energy lead to the formation of large concentration of structural defects in the AAO membranes during its growth through anodization and the AAO layer is grown in a random way having a noncrystalline structure. However, large numbers of oxygen vacancy ($V_O$) defects could be generated spontaneously in the AAO membranes when the oxygen ($O^{2-}$) ions, which are generated from OH$^-$ ions of the electrolyte, migrate through the alumina layer towards the aluminium/alumina interface because of the applied electric field. Additionally, the $C_2O_4^{2-}$, $PO_4^{3-}$ and $SO_4^{2-}$ ions from the electrolyte can also directly get incorporated in the membranes as impurities or by replacing few $O^{2-}$ ions from AAO membranes [18]. Earlier EDAX study of the AAO membranes has shown the presence of very little acidic inclusions in the membranes.

In general, there are three types of $V_O$ defects namely, oxygen vacancies without electron or neutral oxygen vacancies ($F^{++}$ centers), singly ionized oxygen vacancies ($F^-$ centers) and doubly ionized oxygen vacancies ($F$ centers). Here, the presence of $F^{++}$...
centers in AAO can be ruled out because of its instability [24]. Therefore, \( F^+ \) and \( F \) centers are the main oxygen vacancy defects present in AAO membranes, where the \( F^+ \) centers can transform to \( F \) centers by taking electrons from the migrating electron rich ions (O\(^2^-\)) during long term anodization [25]. In this regard, it is believed that the \( F^+ \) center defects are the major kind of structural defects present in the as prepared AAO membranes and their concentration is expected to be high enough than that of the \( F \) centers or acidic inclusions related structural defects.

3.3. EPR spectroscopy study

EPR spectroscopy is an efficient experimental tool to investigate the different kinds of structural defects present in the materials. EPR signal of the AO6, AP6 and AS6 membranes is shown in Fig. 4. The EPR parameter, \( g \) factor is calculated by using the following equation, to obtain an idea about the type of structural defects present in the AAO membranes:

\[
g = h\gamma / \mu_B H
\]

where \( H \) is the magnetic field (gauss), \( \gamma \) is the frequency (Hz), \( \mu_B \) is the Bohr magnetron equal to 9.274 \( \times 10^{-27} \) erg/s/cycle, and \( h \) is Planck’s constant, \( 6.626 \times 10^{-27} \) erg s/cycle. From this calculation an EPR signal close to the value of \( g \approx 1.99 \) appears from all the membranes.

Recently, based on the DFT calculations Özcan et al. [26] have shown that the \( F^+ \) and \( F \) center defects have an even number of electrons and they are EPR-silent singlets. Furthermore, it has also been demonstrated that the \( g \) factor close to the value of 2 can appear because of the \( F^+ \) center defects [25,26]. There are experimental reports in which \( g \) factor close to 2 is attributed to the \( F^+ \) center paramagnetic defects in oxide semiconductors [27,28]. Therefore, our EPR spectroscopy result with \( g \) factor of 1.99 suggests that this signal is originated from the \( F^+ \) center defects present in the AAO membranes. From the intensity of the EPR spectrum of the AAO membrane one can get an idea about the concentration of the defects also. The highest EPR signal from the AO6 membrane suggests that the concentration of the \( F^+ \) center defects present in AO6 is also higher than that of the AP6 and AS6.

3.4. PL spectroscopy study of AAO membranes

Fig. 5 shows the room temperature PL spectra of the AAO membranes prepared by using oxalic, phosphoric and sulfuric acid electrolytes after three different second-stage anodization times. It is evident that all the AAO membranes provide broad luminescence in the visible blue wavelength region. Fig. 5(a) shows that the AAO membranes AO2, AO4 and AO6 exhibit a strong and broad PL emission band around 430 nm. Here, the PL spectrum of AO2 can be fitted into other Gaussian peaks near 475 nm. In the PL spectrum of AO4 there is also another low intensity band around 525 nm, which is not present in AO6. However, in case of the AAO membranes fabricated by using phosphoric acid (AP2, AP4 and AP6) and sulfuric acid (AS2, AS4 and AS6) electrolyte, nearly the similar trend in PL emission spectra is observed. For AP2 the prominent PL emission band appears at about 390 nm and the AP4 and AP6 exhibit PL band around 409 nm. On the other hand, the PL emission band of AS2 is located around 430 nm and that of AS4 and AS6 is centered at 440 nm. However, it is interesting to notice that for all the AAO membranes the PL intensity increases gradually with the increase of the second-stage anodization time. Fig. 5(d) shows the PL emission spectra of the AO6, AP6 and AS6 together for a comparative study. It is evident (Fig. 5(d)) that the intensity of room temperature PL spectra of the AAO membranes gradually decreases from AO6 to AP6 to AS6. The AS6 films provide the weakest luminescence characteristics among the membranes.

3.4.1. The PL mechanism

The light emission characteristics of the AAO membranes have been experimentally investigated by different research groups and there are ambiguities in the reports. Therefore, the understanding of the luminescence mechanism of AAO membranes is still indistinct and evokes lot of debates. In general, the proposed PL emission mechanism of the AAO has been broadly discussed under two major headings: (i) the luminescent centers created from the acidic impurities and (ii) the oxygen vacancy related defect centers present in the AAOs. The PL centers created in the AAO membranes from the oxalic and sulphuric acid impurities have been reported to be the main reason behind the light emission behavior of the AAOs, by some researchers [11,17,18]. On the other hand, major research communities [16,19–21] have explained the luminescence characteristics of AAO membranes on the basis of oxygen vacancy related defect centers (\( F^+ \) and \( F \) centers) grown in the membranes during anodization. Thus, the PL mechanism of the AAOs appears to be more complicated and puzzling till date.

In our experiments the presence of a large number of structural defects in the noncrystalline AAO membranes has been identified by the HRTEM study. Looking into the mechanism of the fabrication of AAO membranes it is expected that the as grown membranes should contain large concentration of structural defects like \( V_O \) defects. Furthermore, the EPR experiment also clarifies the presence of the large concentration of \( F^+ \) center defects in all the membranes. Hence, correlating all these experimental results with the PL measurements it is evident that the \( F^+ \) center defects are responsible for the visible blue light emission from the AAO membranes as in crystalline alumina it has been proved experimentally that the \( F^+ \) center defects can produce a blue PL emission [29,30]. The \( F^+ \) center defects originated during anodization process introduces trap states in the local energy levels of the amorphous AAO membrane [31] and the electronic transitions between the local band edge and the \( F^+ \) center defects results the photon emission from the \( F^+ \) center in the visible blue wavelength region [16,30]. Therefore, the PL emission band observed in this experiment in the blue wavelength region can be attributed to the \( F^+ \) center defects present in the nanoporous AAO membranes. Additionally, the acidic impurities incorporated into the alumina membranes can also be transformed into the luminescent centers and contribute in the light emission. The presence of small amount of the acidic impurities in the membranes is identified.
although their concentration is not large enough to provide significantly intense visible light as that of the F$^+$ centers. More likely, the light emission from the acidic impurity related PL centers can overlap with that of the F$^+$ centers and may be suppressed under the high intensity PL emission peak due to the F$^+$ center defects. In this regard, it is inferred from the experimental evidences that the blue emission from the AAO membranes are mainly attributed to the F$^+$ center defects whereas, the contribution of the acidic impurity related luminescent centers in the PL emission spectra is negligibly small. However, an interesting correlation is found between the EPR and PL spectra measurements of the AO6, AP6 and AS6 membranes, which indicate that PL intensity of the AO6 membrane is maximum (Fig. 5(d)) among the three membranes as the concentration of the F$^+$ center defects in AO6 is highest amongst the AAO membranes. The increase of the intensity of PL band with the increase of anodization time is because of the increase of the concentration of the F$^+$ center defects as the number of the F$^+$

4. Conclusions

In summary, we have successfully fabricated well ordered nanoporous AAO membranes by using oxalic, phosphoric and sulfuric acid electrolytes through controlled electrochemical anodization. All the as prepared membranes exhibit visible blue light emission. The luminescence mechanism of the AAO membranes is demonstrated correlating the PL and EPR spectroscopy measurements with their structural characteristics obtained by the XRD and HRTEM studies. It is found that the noncrystalline AAO membranes are enriched with large concentration of structural defects, mainly F$^+$ center defects, which act as the luminescent centers in AAO membranes to provide visible light emission.
The experimental results indicate that the luminescent centers transformed from the acidic impurities have little contribution to the PL emission spectra of the AAO membranes.

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References