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Effect of etch-treatment upon the intensity and peak position of photoluminescence spectra for anodic alumina films with ordered nanopore array

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Abstract Porous anodic alumina membranes (AAMs) were prepared in oxalic acid and then carried on an etch-treatment in phosphoric acid. Using the etch-treatment the photoluminescence (PL) intensity of AAMs increases by a factor of 1/3. The effect of etch-treatment upon the intensity and peak position of photoluminescence (PL) spectra was investigated. It was found that the intensity of the photoluminescence (PL) spectra increased with the etching time increasing. A PL spectrum can be divided into two subbands with the peak at 434 and 460 nm, respectively. As the etching time prolongs, the intensity of the peak of 434 nm subband increases and that of the 460 nm subband rises firstly and then decreases. It can be explained by that two luminescence centers (F and F^+ centers) coexist in AAMs. F centers are concentrated in the surface layer and F^+ centers are enriched in the depth of pore wall. The increment of the PL intensity comes from the contribution of F^+ photoluminescence centers concentrated in the depth of pore wall in AAMs. This work will be beneficial to improving the photoluminescence intensity and understanding the light-emitting mechanisms for related materials.

Introduction

As an excellent structural material, both the preparation and properties of anodic alumina membranes (AAMs) with ordered nanopore array have been extensively studied [1–4]. Now AAMs have been used as promising templates in fabricating nanostructures and nanomaterials. Various nanomaterials have been encapsulated within the nanopore channels of AAMs to create a revolution in advanced materials because of the potential applications in microelectronics, optoelectronics, and magnetic recording [5–10]. At one time, most investigators were focused on the fabrication of new materials based on AAMs, and the physical properties and application of the AAM itself did not been attached enough importance to. However, the properties of the AAM itself certainly affect the properties of materials fabricated based on the AAM. Fortunately, in recent years, more attention has been paid on the properties, especially the photoluminescence (PL) properties, of the AAM itself. Investigators found that AAM can show blue–green strong photoluminescence [11]. A variety of models have been presented to describe the photoluminescence of AAMs [11–18].

Many authors studied the PL properties of the AAMs formed in oxalic acid ($C_2H_2O_4$), phosphoric acid (H_3PO_4), and sulfuric acid (H_2SO_4) [11–15, 17]. They found that the photoluminescence intensity of AAMs formed in oxalic acid was much stronger than that of AAMs formed in sulfuric acid and phosphoric acid, and other luminescence characteristics of AAMs were also related to the acid used as the electrolyte. Yamamoto et al. [11] reported that alumina formed in oxalic acid solution showed a blue PL band around 470 nm. They proposed that the oxalic impurities incorporated in AAMs can be transformed into luminescent centers by a high-electric-field setup inside the pores, and

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used it for explaining the origin of the PL and the difference of the PL properties of the AAMs prepared in different acids. Soon after, Li et al. [12] reported that the PL of AAMs prepared in sulfuric acid had the same origin as that prepared in oxalic acid. In addition, Du et al. [13] investigated the PL properties of the alumina membranes annealed at a set of temperatures and they attributed the PL to optical transition in individual F^+ center defects. By carefully examining the PL properties of alumina membranes formed in various acids with different concentrations, Huang et al. [17] suggested that there were two kinds of defect centers, F and F^+, which coexisted in the nanopore walls and barrier layer. Green et al. [18] studied the optical properties of porous alumina prepared by electrochemical anodization at temperature from 0 to 20 °C and found that the PL of the samples red-shifts with anodization temperature. They attributed the red-shift to the predominance of the F^+ centers in the samples prepared at a lower temperature.

In brief, many authors investigated the effects of several factors on PL properties of AAMs, such as variety and concentration of electrolyte, anodization temperature and heat-treatment, but etch-treatment. It is well known that many authors succeeded in improving the PL properties of CdTe and InP [19–21] by a etch-treatment. Maybe we can further optimize the PL properties of AAMs by the etch-treatment. In this study, we try to improve the PL properties of the AAMs by using an etching process and make a further understanding for the light-emitting mechanisms of AAMs.

Experiments

The AAMs were prepared through a two-step anodizing electrochemical procedure by using high-purity aluminum foils (≥99.995%) as the anode in oxalic acid. Before anodization, the aluminum foil was degreased in acetone and then electro-polished in a mixture of perchloric acid and ethanol with the volume factor of 1:4 under a constant voltage of 18 V for 3 min. The treated aluminum foil was anodized in 0.3 M oxalic acid electrolyte at 40 V for 10 h. After the first anodization, the foil was immersed in a mixture of 6 wt% phosphoric acid and 1.8 wt% chromium acid at 60 °C for 2 h to remove the alumina layer, which grew at the first step. Then, the aluminum foil was anodized again for 4 h under the same conditions as that of the first step. As a result, the highly ordered porous alumina was formed. At the bottom of the alumina membrane existed the remaining aluminum layer, which was removed by immersing the membrane in a saturated $HgCl_2$ solution. The prepared porous alumina membrane was divided into four samples to ensure the forming condition of the four samples as the same. These samples were named Sample 1, 2, 3, and 4, respectively. After that, the enlargement of pore process was carried on by etching Sample 2, 3, and 4 in 5 wt% phosphoric acid for 10, 20, and 30 min, respectively. After rinsing with deionized water and drying in the air, we obtained four samples with different pore size.

The observation of morphology was handled by SEM (FEI SIRION Field Emission Gun). The PL spectral measurements were carried out using a Hitachi F4500 fluorescence spectrophotometer with a Xe lamp as the excitation light source at room temperature. The excitation wavelength was 350 nm.

Results and discussion

Figure 1 shows the SEM images of an AAM prepared in oxalic acid and three AAMs after etching in phosphoric acid for 10, 20, and 30 min, respectively. A highly ordered nanopore array with a close-packed hexagonal structure can be clearly observed for the four samples. It can be seen that the size of nanopores in the AAM becomes larger and the wall of nanopores becomes thinner with increasing etching time. The evaluated average diameter of nanopores varies from about 40 nm for the as-prepared sample (without etch-treatment) to near 100 nm for the sample etched in phosphoric acid for 30 min. The porosity for the four samples has been measured by digital image processing and the result is listed in Table 1. It can be seen that the porosity of the sample increases as the etching time prolongs.

The PL spectra of the samples without etch-treatment and those with the etching time t = 10, 20, and 30 min have been measured and shown in Fig. 2. Each PL spectrum appears as a broad emission (400–600 nm), which covers almost the whole visible waveband. It can be seen that the emission behaviors of the AAMs are obviously affected by etch-treatment. The intensity of the PL band increases with increasing etching time. The PL intensity of the as-prepared sample is the lowest, and that of the sample etched in 5 wt% phosphoric acid for 30 min, is the highest among four samples. The PL intensity of the AAM increases by a factor of 1/3 after etch-treatment. The position of PL peak is close to 445 nm, from 448 nm (2.76 eV, for Sample 1) to 443 nm (2.80 eV,for Sample 4). There exists a blue-shift of the peak position with increasing etching time. The shift of peak-position is small by comparison with the width of the PL spectrum.

What factor causes the photoluminescence of AAMs, and how the etch-treatment influences on the photoluminescence of AAMs? As we know, porous alumina has an absorption edge in the UV-region [18, 21, 22]. The light from 400 to 600 nm of the PL may be re-absorbed by the porous alumina

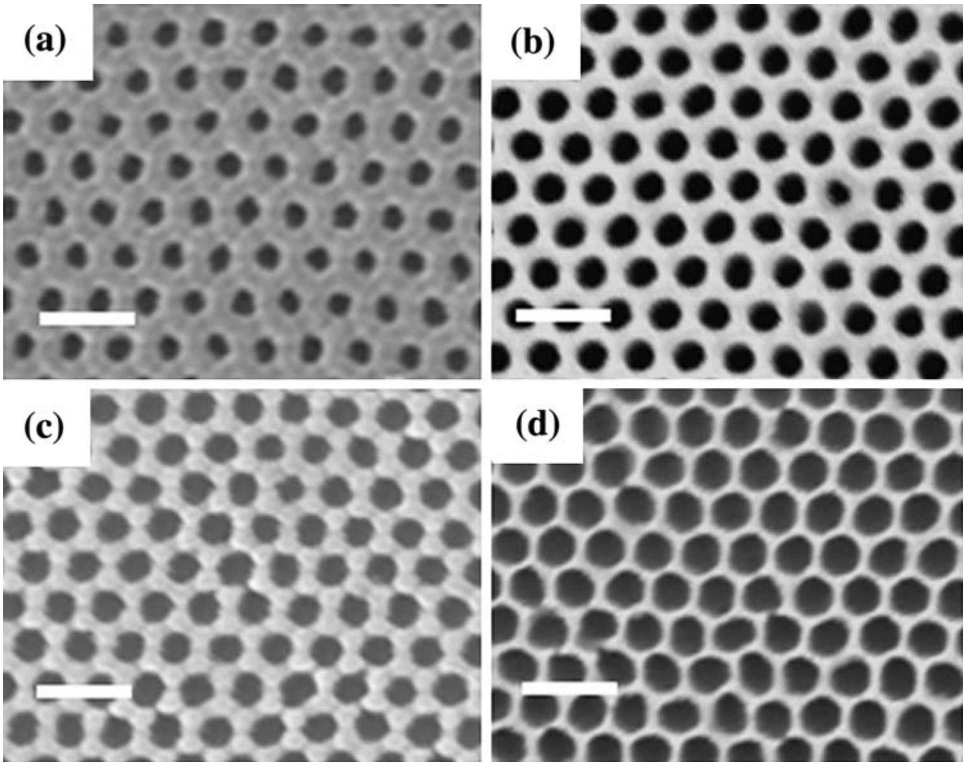

Fig. 1 SEM top-view of porous alumina membranes prepared in oxalic acid. **a** as-prepared; **b** after etching in 5 wt% phosphoric acid for 10 min; **c** for 20 min; **d** for 30 min. The scale is 200 nm

Table 1 Dependence of the porosity upon etching time for the anodic alumina membranes prepared in oxalic acid

Etching time (min)	0	10	20	30
Porosity (%)	19.8	33.2	40.5	61.3

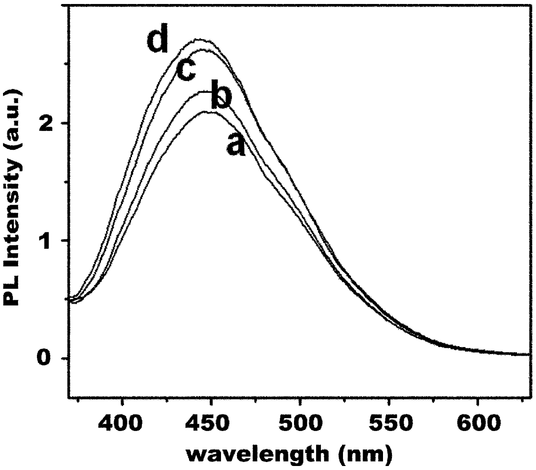

Fig. 2 PL spectra of porous alumina membranes prepared in oxalic acid. (**a**) as-prepared; (**b**) after etching in 5 wt% phosphoric acid for 10 min; (**c**) for 20 min; (**d**) for 30 min

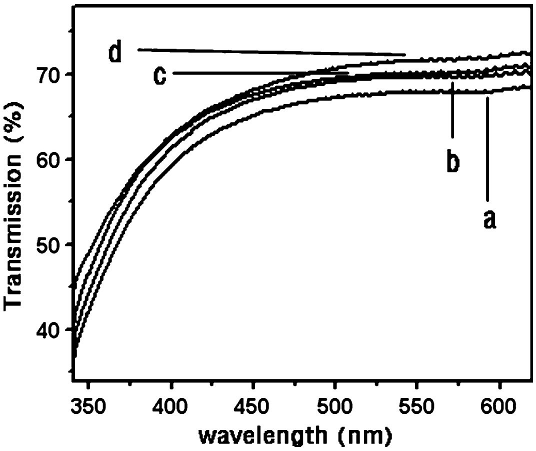

Fig. 3 The transmittance spectra of the porous alumina membranes prepared in oxalic acid. (**a**) as-prepared; (**b**) after etching in 5 wt% phosphoric acid for 10 min; (**c**) for 20 min; (**d**) for 30 min

with different degree. As the etching time increases, if the re-absorption of porous alumina decreases, the PL intensity will increase. To find out the etching treatment on the absorption properties of the membrane, transmittance spectra of the samples were measured. Figure 3 shows the transmittance spectra of the samples without etch-treatment and those with the etching time $t = 10$, 20, and 30 min. It can be found that the transmission of the samples increases slightly as the etching time increases, which indicates that the re-absorption of the samples decreases slightly. However, this change is only less than 5%. So the influence of the light re-absorption by the AAM may lead to a slight increase of the PL intensity, but it cannot be the major reason for the PL intensity of the AAM, which increases by a factor of 1/3 after etch-treatment.

Chang et al. [23] discussed same questions of InP from the point of view of the state density. They investigated the role of the surface recombination velocity in the PL measurement and came to a conclusion, since surface recombination is usually nonradiative, that it make the PL effectively quench and PL intensity reduce. It is well known that the etch-treatment usually decreases the density of surface states [24]. With the etch-treatment proceeding, the original surface is dissolved and the depth of pore wall becomes the new surface. Thus, the density of surface states decreases with increasing etching time. And it is considered that the surface recombination velocity is proportional to the density of surface states [24]. It means that as the etching time increases the surface recombination velocity decreases, the quenching effect created by the surface recombination decreases and then the PL intensity increases as a matter of course.

Many authors studied the origin of the photoluminescence of AAMs and alumina crystal and investigated the influence of etch-treatment on the photoluminescence of AAMs from the point of view of the oxygen vacancy defects at the luminescence centers. In previous literature, the oxygen vacancies were generally considered to be responsible for the PL of alumina [14, 17, 18]. Huang et al. [17] proposed that the strong PL band should consist of two luminescent subbands, which arise from different defect centers, F center and F^+ center, coexisting in the alumina membrane. Du et al. [13] made the electron paramagnetic resonance (EPR) measurements of AAMs and found a single resonance signal with a Lande g value of 2.0085. In general, there may exist three types of oxygen vacancies in AAMs: the oxygen vacancy with two additional electrons (corresponding to F center), without any additional electron (F^{++} center), and with single additional electrons (F^+ center). Since only the F^+ center is single ionized and paramagnetic, F^+ is associated with the EPR signal and the others (F and F^{++}) are not. Therefore, F^+ is a luminescence center in AAMs. In addition, the experiments also proved that the F^+ center can emit a PL peak at about 413 nm (3.0 eV) in crystalline alumina [25, 26]. Huang et al. [17] correlated the PL of AAM with F center and F^+ center and divided the PL spectra into two luminescent subbands. Following the example, we make the Gaussian dividing for each PL spectrum in Fig. 2 and plot them in Fig. 4. It can be seen that each PL peak is divided into two subbands. The two peaks are located at about 434 and 460 nm, respectively. It was proved that the peak of the subband located in the high-energy side of the PL spectrum was related to the F^+ centers and the peak in the low-energy side was related to the F centers [17]. So we can infer that the luminescence centers located at 460 nm are related to the F centers and those located at 434 nm are related to the F^+ centers.

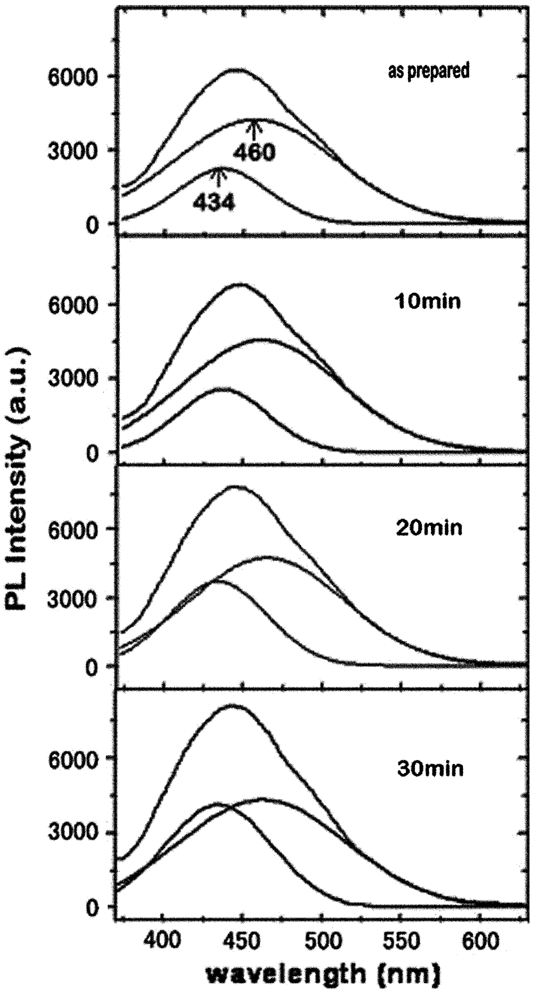

Fig. 4 PL spectra of the porous alumina membranes prepared in oxalic acid for a set of etching time. Each spectrum can be Gaussian divided into two subbands with the peak at 434 and 460 nm, respectively

Figure 4 shows that the peak position of each subband almost does not change, with a shift of less than 2 nm for all four samples. It drops a hint that the PL spectrum indeed results from two types of photoluminescence centers, F and F^+, for the samples with different etching time. Next, we investigate the variation of the intensity of each subband as the sample is etched for different time. Figure 5 shows the dependence of the intensity of peak of F and F^+ subbands upon the etching time. It can be seen that as the etching time prolongs, the intensity of peak at 434 nm subband increases and that of the 460 nm subband rises first and then decreases. How to explain the variation of the intensity of subbands with the etching time? It must be pointed that PL is less stringent about beam alignment, surface flatness, and sample thickness compared with other optical methods of characterization like reflection and absorption, therefore the changes in these factors caused by etch-treatment are not the reason of the PL intensity changes.

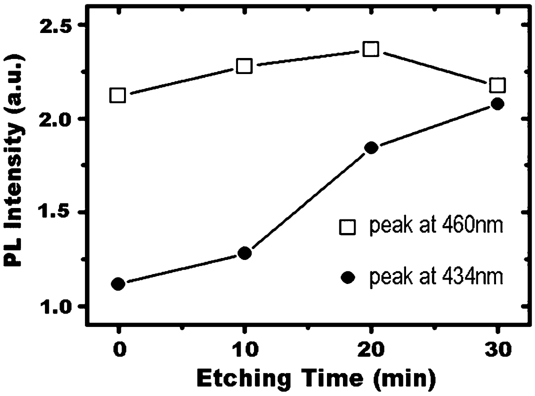

Fig. 5 Dependence of intensity of the peak upon etching time for PL subbands with the peak at 460 (*open square*) and 434 nm (*dark circle*), respectively

The variation of the intensity of subbands with the etching time comes from the variation of the surface state density with the etch-treatment and the different concentration of defect centers between the surface and the depth of pore wall in AAMs.

The variation of the concentration of defect centers with the depth of pore wall can be explained by a model of the growth of anodic alumina [17]. Figure 6 plots a schematic diagram of luminescence center distribution in an AAM. Oxygen in AAMs comes from OH^- in electrolyte solution. Under a steady electric field OH^-gradually migrates to the oxide/metal interface, transfers into O^{2-} and forms new alumina, and the anions in electrolyte solution will drift to the anode. Thus, anions will gradually gather on the surface of alumina membrane and then the oxygen vacancy on the surface of the AAM will easily trap two electrons to become the F center. On the contrary, the oxygen vacancy in the depth of the pore wall will hardly trap electrons and become the F^+ center. As a result, the density of F^+ centers is much larger than that of F centers in the depth of the pore wall, i.e. on the surface of the AAM the density of F centers is larger and in the depth of the pore wall the density of F^+ centers is larger. When the AAM is etching, the surface of the AAM is dissolved gradually. As mentioned above, the luminescence centers of the 460 nm subband is related to F centers and those of the 434 nm subband is related to F^+ centers. To sum up, the intensity of the PL subbands is affected by both the surface state density and the luminescence centers. On the one hand, the density of surface states decreases with increasing etching time, which makes the intensity of both subbands increase; on the other hand as the etching time increases, the concentration of both the luminescence centers decreases, which will make the intensity of both subbands decrease. For the 434 nm subband, the impact of etch-treatment on the F^+ center concentration is small, the effect of decreased surface state density upon the subband intensity always exceeds that of the decreased F^+ center concentration, so the subband intensity increases as the etching time increases. However, for the 460 nm subband, since the density of F centers is larger on the surface of the AAM, the F center concentration greatly decreases as the etching time increases. So the effect of the decreased surface state density upon the subband intensity is larger than that of the decreased F center concentration at the beginning and then lesser, so the intensity increases first and then decreases as the etching time increases.

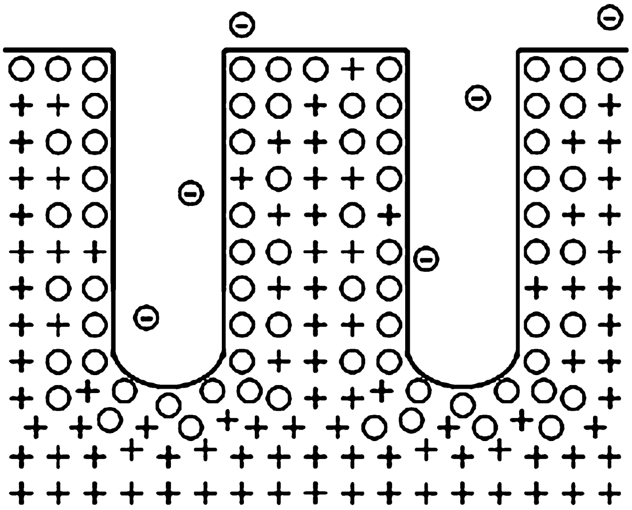

Fig. 6 The schematic diagram of luminescence center distribution in a porous alumina membrane. Anions (*circle with negative sign*) drift to the anode (*alumina membrane*) under an electric field. The density of F centers (*circle*) decreases and that of F^+ centers (*cross*) increases as the depth of pore wall increases

Figure 5 also shows that as compared with the as-prepared sample, the sample etched in phosphoric acid for 30 min the PL intensity of 460 nm subband changes within the range of 10% only, but that of 434 nm subband increases by a factor of 2. It comes to the conclusion that the increment of the PL intensity caused by etch-treatment comes from the contribution of F^+ photoluminescence centers concentrated in the depth of pore wall in AAMs.

Conclusion

The AAMs prepared in oxalic acid possesses much higher intensity of the photoluminescence by comparison with those prepared in phosphoric acid and sulfuric acid. An additional etch-treatment in phosphoric acid can further improve the PL properties of AAMs. The intensity of the PL spectra increased with the increase in etching depth. As the sample is etched in phosphoric acid for 30 min the PL intensity of the AAM increases by a factor of 1/3. The increment of the PL intensity mainly comes from the contribution of F^+ photoluminescence centers concentrated in the depth of pore wall in AAMs.

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