Strong blue emission from anodic alumina membranes with ordered nanopore array

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We have investigated the photoluminescence (PL) from anodic alumina membranes with an ordered nanopore array formed on bulk Al foils. Most of the membranes fabricated by anodization in oxalic acid showed a strong PL peak in the blue. Due to an obvious asymmetry, the PL peak can be Gaussian divided into two bands around 405 and 455 nm, having a slight shift with the sample formed in different acid concentrations. The PL excitation (PLE) spectral examinations and analyses revealed that the two blue PL bands originate from optical transitions in two kinds of different oxygen-deficient defect centers, F (oxygen vacancy with two electrons) and F^+ (oxygen vacancy with only one electron) centers. Their distributions were discussed on the basis of the observed PL and PLE behaviors. Our experimental results improve the understanding of the blue-emitting property of anodic alumina membranes. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1529075]

I. INTRODUCTION

In recent years, porous anodic alumina with an ordered nanopore array has attracted an increasing interest, because of its favorable applications as a template in fabricating nanostructured materials. Among most of the investigations, the formation and morphology of a nanopore array are always topics of research.[1–9] With the development in fabrication conditions, the ordering of nanopores has largely been improved. This will be beneficial to the fabrication of the ordered nanowire and nanodot arrays with applications in future optoelectronic integration.[10–12]

When we use the template to fabricate nanomaterials with a light-emitting property, a problem arises: What is the light-emission property of the template itself? Over the past few years, many models have been presented to describe the photoluminescence (PL) from the alumina membranes,[13,14] but the existing data and explanations are unclear and still in controversy. Recently, Du *et al.*[13] observed a strong blue PL from the alumina membranes on bulk Al and attributed the PL to optical transition in individual F^+ center defects. However, according to the previous investigations and our experiments, this attribution is incomplete and further work is needed to clarify this light-emitting mechanism. In this article, we carefully examine the PL properties of the alumina membranes formed in different acids and acid concentrations. The obtained results indicate that the broad blue PL can be Gaussian divided into two subbands. Spectral analysis suggests that the two bands arise from optical transitions in two kinds of different defect centers, F and F^+ centers,

which coexist in the nanopore walls and barrier layer. This work improves the understanding of the light-emitting mechanism in the alumina membranes.

II. SAMPLES AND EXPERIMENTS

High-purity aluminum foils (99.99%) were used for anodization. Before anodization, the aluminum foil was degreased with acetone and then annealed at 400 °C in N_2 for 1 h in order to increase the grain sizes in the metal and to improve the homogeneity over a large area of the sample. Then, the aluminum foil was electropolished in a mixed solution of perchloric acid and ethanol (1:5 in volume) under a constant voltage of 18 V for 3 min. To get ordered nanopore array,[3,5] annealing and electropolishing are necessary. Anodization was conducted under a constant voltage of 40 V. The electrolyte was phosphoric acid (0.87 M) or oxalic acid (0.5, 0.23, and 0.1 M). To get an ordered nanopore array, we used two-step anodizing process.[11,12] Al foil was anodized for 2 h as the first step and followed by immersion into a mixture of 5 wt % phosphoric acid and 1.8 wt % chromium acid (1:1 in volume). The temperature of the mixed solution was kept at 80 °C. After 30 min, the alumina layer, which grew at the first step, was removed and the surface of the foil becomes bright. Since the intensity of light emission depends on thickness of the membrane, anodizing time for the second step was set to be longer, about 24 h. Other experimental conditions were kept unchanged. During anodization, the current–time ($I-t$) curves were recorded to compare the influence of acid concentrations on anodizing process. The scanning electron microscope (SEM) images of the sample surfaces were obtained on JSM-6300 equipment of the JEOL company. The PL and PL excitation (PLE) spectral measure-

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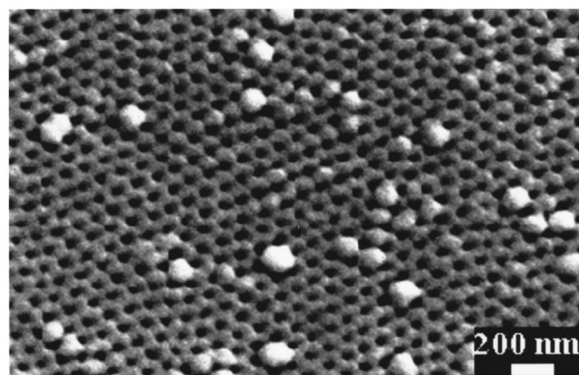[a)]Author to whom correspondence should be addressed; electronic mail: hkxlwu@nju.edu.cn

FIG. 1. The SEM micrograph of the alumina membrane obtained by anodization of Al foil in 0.5 M oxalic acid.

ments were carried out on a Hitachi F4040 fluorescence spectrophotometer. All spectra were obtained at room temperature.

III. EXPERIMENTAL RESULTS AND ANALYSES

Figure 1 shows the SEM image of the sample anodized in 0.5 M oxalic acid. A highly ordered nanopore array with a polycrystalline pore structure can clearly be observed in Fig. 1.[5] The array shows a density-patched hexagonal structure. Similar SEM images can also be obtained in other samples anodized in oxalic acid solutions of different concentrations, indicating that the currently used anodization is appropriate for fabricating porous alumina membranes with a highly ordered nanopore array.

The PL spectra of the alumina membranes formed in both 0.5 M oxalic acid and 0.87 M phosphoric acid are shown in Fig. 2(a). It can be seen that under an excitation of the 280 nm line of a Xe lamp, the membrane formed in oxalic acid displays a strong blue PL peak at 440 nm, while that formed in 0.87 M phosphoric acid only has a very weak emission. This result indicates that the electrolyte has a large influence on the light-emitting property of anodic alumina
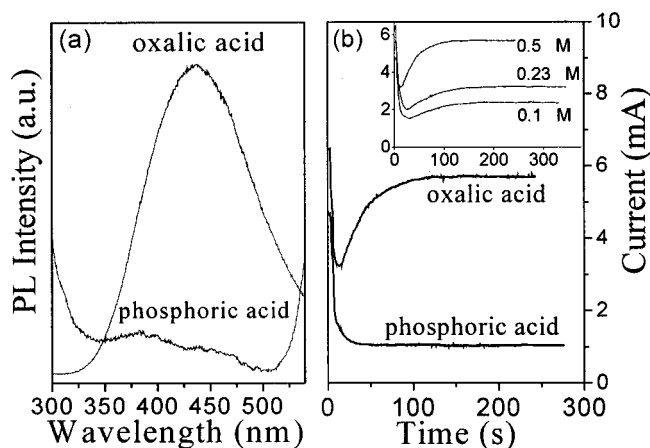

FIG. 2. (a) The PL spectra of the alumina membranes obtained by anodization of Al foils in oxalic acid and phosphoric acid. (b) The $I-t$ curves of anodic processes in oxalic acid and phosphoric acid. The inset shows the $I-t$ curves of the alumina membranes formed in 0.5, 0.23, and 0.1 M oxalic acids.

membrane. We found that the ordered nanopore array can also be obtained in the samples anodized in sulfuric acid, but no obvious PL was observed.[13] Therefore, there is no certain relationship between PL properties and the ordering of nanopores. Figure 2(b) shows the corresponding $I-t$ curves of the two kinds of membranes. In the initial stage, a sudden decrease of the current means that the Al oxide begins to grow and, simultaneously, nanopores start to form. After about 100 s, the initial stage ends and the current becomes stable. The dissolution of the alumina at the electrolyte/oxide interface and its formation at the oxide/metal interface are balanced. In the anodizing process of the two samples, we note that the profiles of the $I-t$ curves in the initial stage have a large difference, but a long-time anodization of 24 h should naturally eliminate the influence of this difference on membrane growth by dissolving the thin surface layer. In the steady growth stage, although the voltages are all set at 40 V, the value of the current is different in different electrolytes. The current is much larger in the sample anodized in 0.5 M oxalic acid than that in 0.87 M phosphoric acid. According to theoretical model of the growth of anodic alumina,[7–9] oxygen in the alumina comes from OH^- in electrolyte solution. With the alumina growth, OH^- gradually migrates to the oxide/metal interface to transfer into O^{2-} and then to form new alumina. Therefore, the concentration of oxygen vacancies is inversely proportional to that of OH^- in the solution. Since the presence of oxygen vacancies has generally been considered to be responsible for the PL of anodic alumina,[13,14] large PL intensity corresponds to a large concentration of oxygen vacancies. Correspondingly, the OH^- concentration is low. In the samples anodized in oxalic acid, the current is larger and thus the consummation of OH^- is more. This will lead to the OH^- concentration being lower in the solution. So, the alumina membrane formed in 0.5 M oxalic acid has more oxygen vacancies. As a result, the PL intensity is stronger. In the present experiments, we also found that different electrolytes can lead to different anodic currents and different microstructural features of the formed alumina membranes. This affects the local environment of the oxygen vacancies and, hence, results in slight change of the observed PL peak positions.

Figure 3(a) shows the PL spectra of the alumina membranes formed in 0.5, 0.23, and 0.1 M oxalic acids, taken under an excitation of the 280 nm line of a Xe lamp. It can be seen that the strong PL is obviously asymmetrical. In previous literature,[13,15] the strong PL was only considered to be single peak and attributed to optical transition in a kind of defect center, F^+ center. From our present results, this attribution seems to be incorrect. To clarify its origin, each PL peak is Gaussian divided into two luminescent bands at about 405 and 455 nm, with a shift of less than 10 nm in different samples. The intensity of the 455 nm band relative to the 405 nm band increases with the used electrolyte concentration, indicating that the two bands have different origins. To identify the defect features related to the two PL bands, the PLE spectra monitored at 405 and 455 nm were examined and the corresponding results are shown in Figs. 3(b) and 3(c). It can be seen that the PLE peaks are located at different positions. In the sample anodized in 0.1 M oxalic
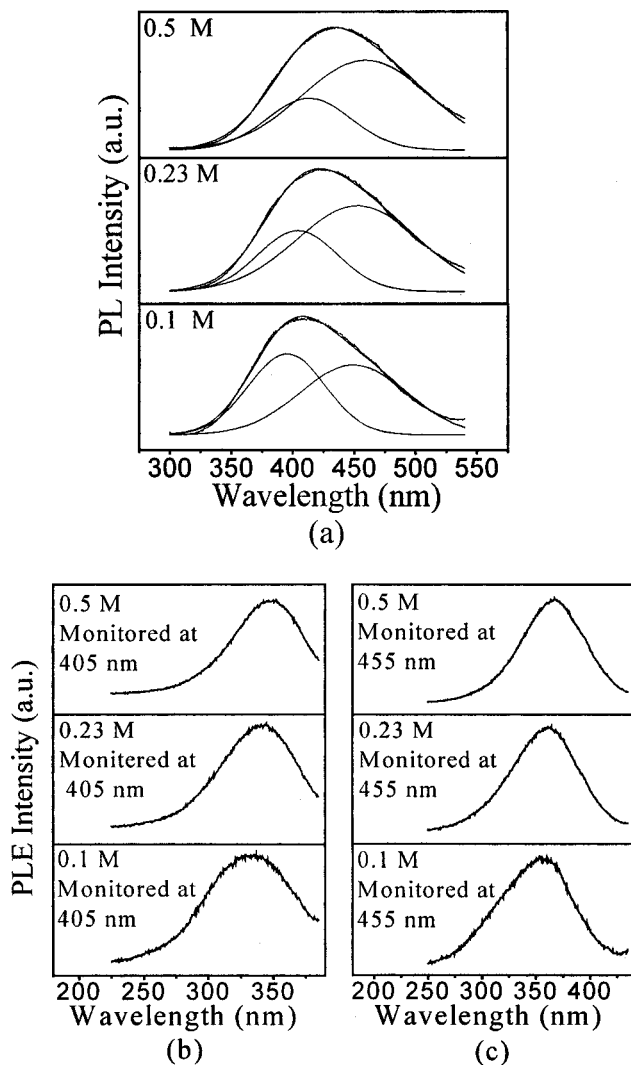
FIG. 3. (a) The PL spectra of the alumina membranes obtained by anodization of Al foils in 0.5, 0.23, and 0.1 M oxalic acids. Each spectrum can be Gaussian divided into two PL bands at 405 and 455 nm. (b) and (c) The corresponding PLE spectra monitored at 405 and 455 nm.

acid, the shift of the PLE peak positions reaches 25 nm between the two spectra at the bottom of Figs. 3(b) and 3(c). This shift cannot be caused by single kind of defect center. So, we believe that the strong PL band should consist of two luminescent bands. They arise from different defect centers coexisting in the alumina membrane.

IV. LIGHT-EMITTING MECHANISMS

From the aforementioned experimental results and analyses, we have learned that the strong blue PL spectrum consists of two bands, which arise from two kinds of different luminescent centers. Previously, many investigations have shown that one defect center is the F^+ center (oxygen vacancy with single electron).[13,14] Electron paramagnetic resonance (EPR) results exhibit a single resonance signal with a Lande g value of 2.0085.[13] The single ionized and paramagnetic F^+ center is closely associated with the observed EPR signal. In crystalline Al_2O_3, it has experimentally been proven that the F^+ center can emit a PL peak at

about 413 nm (3.0 eV).[15,16] Therefore, we can infer that the peak in the high-energy side of the currently obtained PL spectrum is related to the F^+ centers. The PL peak in the low-energy side should have another origin (from another kind of defect centers) due to its different PL behavior. From the single peak feature of the measured EPR spectra, we can infer that the other defect center is not paramagnetic. It may trap zero or two electrons. However, the oxygen vacancy without an electron (F^{++} center) is not stable.[17] Hence, we can rule out the possibility for the low-energy PL peak to be connected with the F^{++} center. In addition, it has also been reported that there exists a large number of F centers (oxygen vacancy with two electrons) in crystalline alumina.[16] The F center is not paramagnetic. According to the behaviors of oxygen vacancies in an anodic alumina membrane, we may infer that there exist three kinds of oxygen vacancies (F, F^+, and F^{++}) or their combinations in the membrane. For simplicity, similar to previous investigation,[13] we do not consider the combination defects, the most possible defect, which leads to the low-energy PL band, would be the F center. Draeger *et al.*[16] have reported a PL peak at 2.9 eV (430 nm) in crystalline alumina. This PL peak was suggested to be
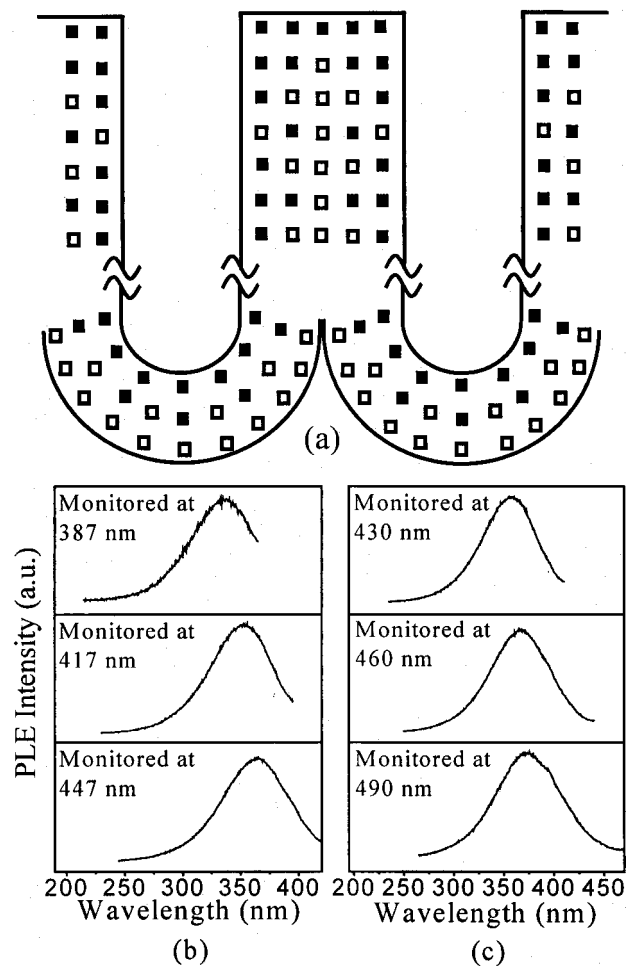

FIG. 4. (a) A model for distribution of the F (dark square) and F^+ (open square) centers in the alumina membranes. The densities of the F and F^+ centers decrease and increase by increasing the depth of pore walls, respectively. (b) and (c) The PLE spectra of the alumina membrane formed in 0.5 M oxalic acid, taken by monitoring at different emission wavelengths.

a transition between energy levels of the F center. Considering the microstructural difference between crystalline Al_2O_3 and amorphous alumina,[14] we believe that the low-energy PL peak is intimately connected with the F centers.

From Fig. 3(a), we have seen that the intensity of the 455 nm band relative to the 405 nm band increases with the concentration of oxalic acid. This implies that the relative densities of the F and F^+ centers have a tendency to increase and decrease with increasing the concentration of oxalic acid, respectively. This tendency can be explained by analyzing the growth process of the alumina membrane. When using 0.5 M oxalic acid as an electrolyte, the current is larger and more charge carriers move to the alumina. The oxygen vacancies are apt to trap two electrons and, therefore, the density of the F center is larger. On the contrary, when using 0.1 M oxalic acid as an electrolyte, little current makes many oxygen vacancies only trap one electron. As a result, the density of the F^+ centers is larger. So the densities of the two kinds of defect centers are different in different samples. Furthermore, the distribution of the two kinds of defects in the anodic alumina membrane should also not be uniform, because under an action of the force of electric field, anions will drift to the anode. Therefore, some anions (negative charges) will gather on the surface of alumina membrane. The oxygen vacancies located on the surface can easily trap two electrons to become the F centers. According to this analysis, a defect-distributed model in the membrane can be presented in Fig. 4(a). The density of the F centers is the largest on the surface, followed by a gradual decrease with an increase in the pore wall depth. The situation of the F^+ centers is just reversed. To seek support for this model, we examined the PLE spectra of the membrane formed in 0.5 M oxalic acid under different monitored wavelengths around 417 and 460 nm and the corresponding results are shown in Figs. 4(b) and 4(c). We can see from these PLE spectra that the PLE peak position has a blueshift by decreasing the monitored wavelength, indicating that the distribution of the defect centers in the membrane is inhomogeneous.[18] This inhomogeneity reflects the distribution of the F and F^+ center densities in the pore walls, in agreement with our model.

V. CONCLUSION

We have investigated the PL spectra from anodic alumina membranes with an ordered nanopore array. The membranes formed in oxalic acid show a strong blue emission, which consists of two luminescent bands. Spectral examinations and analyses suggest that the two luminescent bands arise from two kinds of different defects (F and F^+ centers), rather than only one kind of defect center, F^+ center, as reported previously. Their distribution in the pore walls has modally been discussed. The present experiments and results will be beneficial to the understanding of light-emitting mechanisms in relative materials.

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