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On the origin of light emission from porous anodic alumina formed in sulfuric acid

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Abstract

We have investigated the photoluminescence (PL) property of porous anodic alumina membranes (PAAMs) formed on bulk Al foils in 0.3 M sulfuric acid. Different from that from the PAAMs formed in oxalic acid, the obtained PL spectra show two emission bands which have different origins. One centered at ~465 nm (α-band) weakens its intensity in the PAAM annealed in O_2 and is thus attributed to optical transition in oxygen vacancies. The other in the blue (β-band) redshifts with increasing excitation wavelength. On the basis of spectral examinations and analyses, we ascribe the β-band to radiative recombination of carriers in the isolated hydroxyl groups at the surface of the pore wall, whereas the photogeneration of carriers takes place in oxygen vacancies in the pore wall. This work improves the understanding of the light-emitting property of the PAAMs formed in sulfuric and oxalic acid.

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1. Introduction

In recent years, porous anodic alumina membrane (PAAM) with ordered nanopore array has attracted an increasing interest due to its simple preparation technique and favorable applications as a template in fabricating nanostructured materials [1–3], such as Eu_2O_3 nanotube and Ge nanorod array [4,5]. Of all the fabricated materials, their light-emitting properties have become a subject of many experimental and theoretical investigations due to their applications in nanoelectronics and optoelectronics. However, it was well known that the PAAM itself has a photoluminescence (PL) feature and an energy transfer process could take place from the membrane to embedded nanomaterial [6,7]. Therefore, a detailed knowledge about the PL behavior of the PAAM itself is of technological importance from the viewpoint of application. Over the past years, most of the investigators have drawn their attention to the light-emitting property of the PAAM formed in oxalic acid and revealed the origin of a blue emission [6,8,9]. However, little has been done in PL property of the PAAMs formed in sulfuric acid. Generally, the PL from the PAAM formed in sulfuric acid was simply considered to have the same origin as that in oxalic acid [6]. In the present work, we carefully investigate the light emission property of the PAAMs formed in sulfuric acid. Two emission bands, different from those in the PAAMs formed in oxalic acid, are observed. Their origins are discussed on the basis of spectral examinations and analyses. This work improves the understanding of the light emission mechanism in the PAAMs formed in sulfuric acid.

2. Experiments

High-purity Al foils (99.99%) were used to fabricate the PAAMs. Anodization was conducted in a 0.3 M sulfuric acid solution under a DC voltage of 25 V. The electrolyte was maintained at 5 °C and mechanically stirred. Two-step anodic process, in which anodic times were set for 3 and 2 h, respectively, was adopted to get the PAAM with ordered nanopore array [10]. Electron paramagnetic resonance (EPR) spectra were obtained with a Bruker EMX-10/12 spectrometer operated in X band. PL and PL excitation (PLE) spectra were taken, respectively, on 48,000 DSCF fluorescence spectrophotometer (SLM Company) with the 325 nm line of He–Cd laser

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as excitation source and FluoroMax-2 fluorescence spectrophotometer (Jobin-Yvon Company) with a 150 W Xe lamp as light source. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 displays the PL spectra of the PAAMs formed in oxalic acid and sulfuric acid, taken under excitation with the 325 nm line of a He–Cd laser. Here, we first mention that the PL intensity of the PAAM formed in oxalic acid is much higher than that in sulfuric acid. The current PL intensities in Fig. 1 have been normalized. We can see from Fig. 1 that the two spectra have different lineshapes. The PL spectrum of the PAAM formed in oxalic acid shows a band at 435 nm with a full width at half maximum (FWHM) of 105 nm. According to our previous investigation [8], this broad band is connected with two kinds of oxygen vacancies (F and F^+ centers). However, the PAAM formed in sulfuric acid only shows a narrow band at 403 nm with a FWHM of 65 nm, indicating a different origin in optical emission. To explore the difference, the EPR spectra were measured and the corresponding results are exhibited in the inset of Fig. 1. From the EPR result of the PAAM formed in oxalic acid, we can obtain a Lande g value in Zeeman interaction term to be 2.0081. This EPR signal has previously been reported and attributed to F^+ center [6]. Interestingly, no EPR signal is observed for the PAAM formed in sulfuric acid, indicating that the corresponding luminescent centers are not paramagnetic. Hence, we come to the conclusion that the light emission processes in the two samples are quite different.

Unfortunately, the PL intensity of the PAAM formed in sulfuric acid is very weak under the excitation lines of a Xe lamp. We found that after the PAAM is annealed in N_2 at 400 °C for 2 h, the PL intensity is largely increased and can be detected via a Xe lamp excitation, as shown in the highest curves of Fig. 2(a) and (b). This result rules out the possibility of emission being connected with anion impurities (the PL enhancement mechanism will be discussed later). Here, we should mention that we have also examined the EPR spectrum of the annealed membrane and no signal was detected. Fig. 3(a) shows the PL spectra of the annealed sample. Under excitation with the 270 nm line, a broad band can be observed with a peak position at ~465 nm. When excited with the 290 nm line, a shoulder appears at ~390 nm. With increasing excitation wavelength, the ~390 nm band redshifts and its intensity increases, and meanwhile the intensity of the 465 nm band decreases relative to that of the 390 nm band. Under excitation with the 390 nm line, only one emission band appears at 470 nm. Fig. 3(b) shows the PLE spectra of the annealed PAAM, taken under different monitoring wavelengths. It can be seen that with increasing the monitored wavelength, a strong PLE band redshifts and meanwhile a weak shoulder appears at ~280 nm. To simplify our description, the PL band, which is pinned at 465 nm, is labeled as α-band, while the other band, which redshifts with increasing excitation wavelength, is named as β-band.

To disclose the origins of the two bands, we slightly etched the annealed PAAM sample in 6 wt% H_3PO_4 at 25 °C for 5 min to remove the surface layer of the pore wall (less than 1 nm)

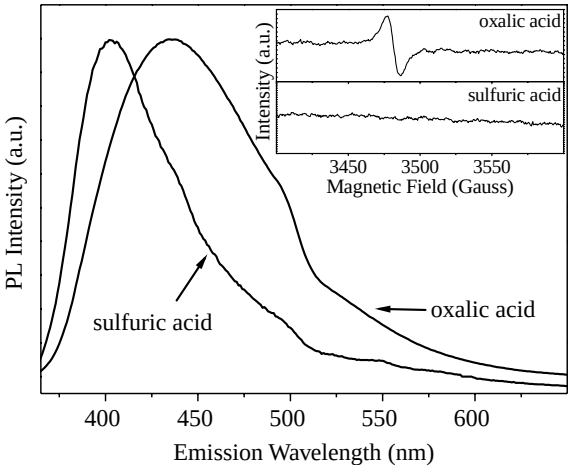

Fig. 1. PL spectra of the PAAMs with normalized intensities formed in oxalic acid and sulfuric acid, taken under excitation with the 325 nm line of a He–Cd laser. The inset shows the corresponding EPR spectra.

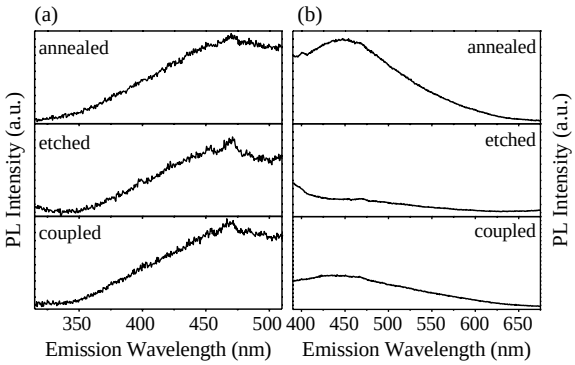

Fig. 2. (a) PL spectra of the annealed, etched, and coupled PAAM samples (the α-band), taken under excitation with the 270 nm line of a Xe lamp. (b) PL spectra of the annealed, etched, and coupled samples (the β-band), taken under excitation with the 360 nm line of a Xe lamp.

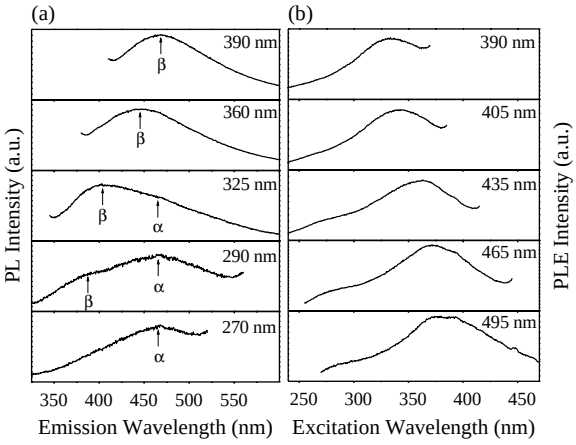

Fig. 3. (a) PL spectra of the PAAM formed in sulfuric acid, taken under excitation with different wavelengths of a Xe lamp. (b) PLE spectra of the PAAM formed in sulfuric acid, taken by monitoring at different emission wavelengths.

[11]. The α- and β-bands from the etched sample are demonstrated in the middle curves of Fig. 2(a) and (b), respectively. One can see that the α-band slightly decreases its intensity, whereas the β-band can hardly be observed. The PL result further proves the α- and β-bands to have different origins and suggests that the luminescent centers responsible for the two PL bands are local at the interior and surface of the pore wall, respectively. To identify the origin of the β-band, we draw our attention to the surface composition of the PAAM. In the previous studies on the PAAMs [12], a surface layer consisting of a mixture of boehmite [AlO(OH)] and alumina has been proposed. The presence of boehmite was considered to be a result of incorporation of water, which leads to the formation of monohydrate in amorphous alumina. Therefore, many hydroxyl (OH) groups should exist at the surface of the pore wall. Recently, blue/green emission at ∼2.7 eV (460 nm) from both metal oxidized films and SiO_2 absorbed with OH groups has also been reported and its maximal intensity appears in such samples with heating to ∼400 °C, corresponding to the dehydroxylation of nearly half of OH groups [13,14]. Thus, the 2.7 eV PL band has been attributed to optical transition in the isolate OH groups [13,14]. Under higher annealing temperature, further dehydroxylation of OH groups can cause a remarkable decrease of PL intensity. This phenomena is consistent with our observation from the PAAM annealed at 450 °C. Considering similar microstructure and annealing behavior, we believe that the β-band in the PAAM should also arise in the isolate OH groups [13,14]. To support our deduction, we used a coupling agent $[(CH_3O)_3Si(CH_2)_3NH_2]$ to eliminate partial OH groups on the surface by immersing the annealed PAAM sample in a dilute toluene solution of coupling agent and examined the PL spectra of the coupled sample. We found that the intensity of the β-band is dramatically reduced, but no obvious change is observed for the α-band [see the lowest curves in Fig. 2(a) and (b)]. This result supports our conclusion that the isolated OH groups are responsible for the β-band. However, the α-band should have other origin.

The inset in Fig. 4 exhibits annealing behavior of the α-band. Obvious decrease in PL intensity of the PAAM annealed in O_2 indicates that the α-band is related to oxygen vacancies which are determined by the growth process of the PAAM [15]. Similarly, the intensity enhancement in the sample annealed in N_2 should be due to increased oxygen vacancies caused by Al oxidization [6]. Previously, Pogatshnik et al. [16] reported electron transfer process from F_2 (4.8 eV) to F_2^{2+} center (2.7 eV) in sapphire under ultraviolet excitation. Considering microstructural difference between sapphire and the PAAM, the α-band and the ∼280 nm PLE band are believed to arise from optical transitions in F_2^{2+} and F_2 centers, respectively. However, surprisingly, the β-band also shows a similar annealing behavior, as displayed in Fig. 4, indicating that the β-band should also be connected with oxygen vacancies. According to our previous investigation [8], the PLE band at ∼370 nm from the PAAM formed in oxalic acid originates in F center. In addition, in the study of emission from OH groups absorbed on SiO_2, the photoexcitation of carriers was suggested to be in the defect centers in SiO_2 network [14].

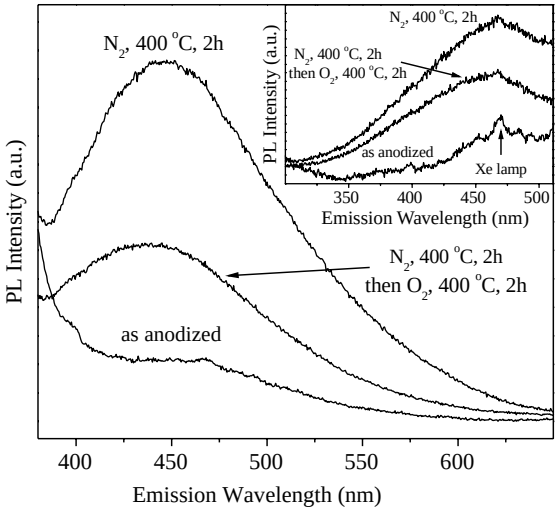

Fig. 4. Annealing behavior of the β-band taken under excitation with the 360 nm line of a Xe lamp. The inset shows annealing behavior of the α-band taken under excitation with the 270 nm line of a Xe lamp. The narrow peak in the as-anodized sample is background signal from Xe lamp.

Moreover, in alkali halides, a tight relationship between F centers and hydroxyl groups and their overlapping in energy levels have been disclosed [17,18]. Therefore, we believe that the photogeneration of carriers in F centers and then radiative combination in OH groups may be responsible for the β-band. Here, we would like to point out that the redshift of the β-band with increasing excitation wavelength generally reflects a distribution of energy levels caused by different local environments (strain, structure, etc.) of luminescent centers. In the current samples, OH groups are localized at the pore walls with different depths beneath the membrane surface and can thus be understood to have very different local environments. This is the reason which leads to the β-band redshift.

4. Conclusion

We have investigated the PL property of the PAAM formed in 0.3 M sulfuric acid. Two PL bands are identified. One is the α-band with the emission center at ∼465 nm, which is connected with oxygen vacancies in the membrane. The other is the β-band in the blue which redshifts with increasing the excitation wavelength. We attribute the β-band to optical transition in the isolate OH groups at the surface of the pore wall, while the photogeneration of carriers occurs in F centers in the pore wall. This work improves the understanding of the light emission property of the PAAM formed in sulfuric acid.

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References

[1] R.C. Furneaux, W.R. Rigby, A.P. Davidson, Nature 337 (1989) 147.
[2] H. Masuda, K. Fukuda, Science 268 (1995) 1466.
[3] O. Jessensky, F. Müller, U. Gösele, Appl. Phys. Lett. 72 (1998) 1173.
[4] G.S. Wu, L.D. Zhang, B.C. Cheng, T. Xie, X.Y. Yuan, J. Am. Chem. Soc. 126 (2004) 5976.
[5] Y.F. Mei, Z.M. Li, R.M. Chu, Z.K. Tang, G.G. Siu, R.K.Y. Fu, P.K. Chu, W.W. Wu, K.W. Cheah, Appl. Phys. Lett. 86 (2005) 021111.
[6] Y. Du, W.L. Cai, C.M. Mo, J. Chen, L.D. Zhang, X.G. Zhu, Appl. Phys. Lett. 74 (1999) 2951.
[7] Y.L. Shi, J. Wang, H.L. Li, Appl. Phys. 75 (2002) 423.
[8] G.S. Huang, X.L. Wu, Y.F. Mei, X.F. Shao, G.G. Siu, J. Appl. Phys. 93 (2003) 582.
[9] Y. Li, G.H. Li, G.W. Meng, L.D. Zhang, F. Phillipp, J. Phys, : Condens, Matter 13 (2001) 2691.
[10] H. Masuda, M. Satoh, Jpn. J. Appl. Phys., Part 2 35 (1996) L126.
[11] Y. Yamamoto, N. Baba, S. Tajima, Nature (London) 289 (1981) 572.
[12] J.W. Diggle, T.C. Downie, C.W. Goulding, Chem. Rev. 69 (1969) 365 and reference therein.
[13] H. Tamura, M. Rückschloss, T. Wirschem, S. Veprek, Thin Solid Films 255 (1995) 92.
[14] M. Rückschloss, T. Wirschem, H. Tamura, G. Ruhl, J. Oswald, S. Veprek, J. Lumin. 63 (1995) 279.
[15] J. Siejka, C. Ortega, J. Electrochem. Soc. 124 (1977) 883.
[16] G.J. Pogatshnik, Y. Chen, B.D. Evans, I.E.E.E. Tran, Nucl. Sci. NS-34 (1987) 1709.
[17] L. Gomes, S.P. Morato, Phys. Rev. B 55 (1997) 8743.
[18] L. Gomes, F. Luty, Phys. Rev. B 30 (1984) 7194.