

*Rapid communication***Strong ultraviolet and violet photoluminescence from Si-based anodic porous alumina films**

J.H. Wu, X.L. Wu*, N. Tang, Y.F. Mei, X.M. Bao

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, P.R. China

Received: 24 July 2000/Accepted: 24 February 2001/Published online: 3 May 2001 – © Springer-Verlag 2001

Abstract. We have investigated photoluminescence (PL) from Si-based anodic porous alumina films formed by real-time controlled anodization of electron-beam evaporated Al films. As-anodized samples show three strong PL bands at 295, 340, and 395 nm. These bands blueshift and their intensities decrease after the samples are annealed. When the annealing temperature increases to 1000 °C, the blueshift becomes specially pronounced and meanwhile the structures of the films develop toward crystalline Al₂O₃. Based on discussions on the thermal annealing behaviors of the PL and PL excitation spectra, we suggest that optical transitions in oxygen-related defects, F⁺ (oxygen vacancy with one electron) centers, are responsible for the observed ultraviolet and violet PL.

PACS: 68.55.Ln; 78.55.Mb

In recent years, there has been an increasing interest in self-organized anodic porous alumina (PA) films as templates for fabricating nanostructured materials [1–7]. However, little work has been focused on the optical properties of self-organized PA film itself. Previous investigations [8, 9] on anodic PA films grown on bulk Al indicate that these films have blue and violet emissions. Therefore, we may expect to obtain excellent light-emitting properties from Si-based anodic PA films. As a kind of Si-based material, PA film can be used as a host or a template for fabricating various nanostructured materials. Alumina can provide a high confined potential to some embedded semiconductor nanocrystals, and thus efficient light emission can be obtained from the materials. On the other hand, alumina with a high selective etching property is well suited for use as a mask in Si patterning, so that a structure with a size smaller than 10 nm can be fabricated by using self-organization. Anyway, Si-based anodic PA film is a promising material in optoelectronics.

Based on the above-mentioned applications, in this letter we investigate for the first time the photoluminescence (PL)

properties of Si-based PA films. Some new and significant results were obtained and we will discuss all the results.

The substrates used in this work were *p*-type (100)-oriented Si wafers with a resistivity of 5 Ω cm. Al film with a thickness of about 400 nm was deposited onto Si wafer using the electron beam evaporation technique. Prior to deposition, the wafer was rinsed in acetone and methanol and then etched in dilute HF solution to remove native oxide, and this was followed by further rinsing in deionized water. To obtain the Si-based anodic PA films, a real-time controlled anodization method was employed, based on monitoring of the anodic *I*-*t* curve. The controlled process has been published in the literature [10]. Anodization with a platinum plate as a cathode was carried out in 15 wt. % sulfuric acid at 5 °C under a constant dc voltage of 20 V. After anodization, the samples were rinsed thoroughly in deionized water and dried in N₂ gas. Finally, the samples were annealed at 400, 800, 1000, and 1100 °C in N₂ and air, respectively. PL and PL excitation (PLE) spectra were measured on a Hitachi F4040 fluorescence spectrophotometer. X-ray diffraction (XRD) measurement was carried out on a Rigaku 3015-type single crystal diffractometer using Cu K_α radiation. The X-ray wavelength is 0.154 nm.

Figure 1(a)–(d) show the PL spectra of the anodic PA films annealed at 400, 800, 1000, and 1100 °C in N₂ for 30 min, respectively, measured with an excitation of the 240-nm line of a Xe lamp. As a comparison, the PL spectrum of the as-anodized film is also presented in Fig. 1(e). Obviously, these PL spectra all show three strong PL peaks. For the sample annealed at 400 °C, their positions are at 295, 340, and 395 nm, consistent with those in the as-anodized sample. These PL peaks slightly blueshift in the samples with annealing temperatures (*T*_a) of 800 °C. However, in the sample with *T*_a = 1000 °C, the blueshift becomes especially pronounced. Their positions were at 270, 310, and 365 nm, respectively. The three PL peaks further blueshift to 263, 300, and 356 nm in the sample with *T*_a = 1100 °C. In addition to the blueshift, the intensities of the three peaks also decrease with increasing *T*_a. Figure 2(a) and (c) show the PL spectra of the samples annealed at 800 °C in N₂ and air for 30 min, respectively. Obviously, the positions of these PL peaks remain unchanged

*Corresponding author. (E-mail: hkxlwu@netra.nju.edu.cn)

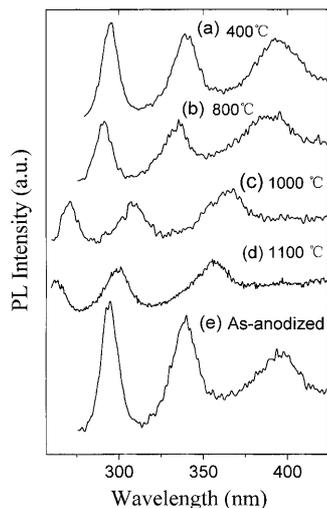


Fig. 1. PL spectral evolution of Si-based PA films as a function of T_a in N_2 for 30 min

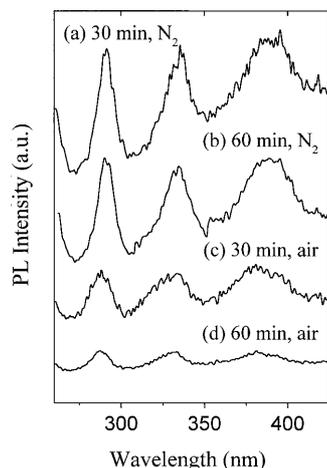


Fig. 2. PL spectra of Si-based PA films annealed at 800 °C in N_2 for (a) 30 and (b) 60 min and in air for (c) 30 and (d) 60 min, respectively

with annealing atmosphere, but the intensity is weakened in the sample annealed in air. This result implies that the existence of oxygen in the annealing atmosphere will reduce the PL intensities. Therefore, the radiative centers leading to the observed PL are oxygen-deficient. This point can also be seen in Fig. 2(b) and (d), which exhibit the dependence of the PL spectra on the annealing time. If we increase the annealing time to 60 min, the PL intensities are also reduced. According to the obtained PL results, we may infer that the anodic oxide film on the Si wafer is stable in structure during heat treatment because the positions of the PL peaks hardly change except for a slight reduction in their intensities.

To identify the origins of these PL peaks, we examined the XRD spectra of our samples. Some typical results from the samples annealed in N_2 are presented in Fig. 3(a)–(c). Spectrum (a) from the sample with $T_a = 800$ °C is similar to spectrum (d) from the as-anodized sample, and no diffraction peaks related to anodic PA films are observed except for those from the Si substrate. As T_a increases to 1000 °C, a new diffraction peak appears at $2\theta \approx 47^\circ$. The peak consists of two sharp peaks. From their positions, we can infer that

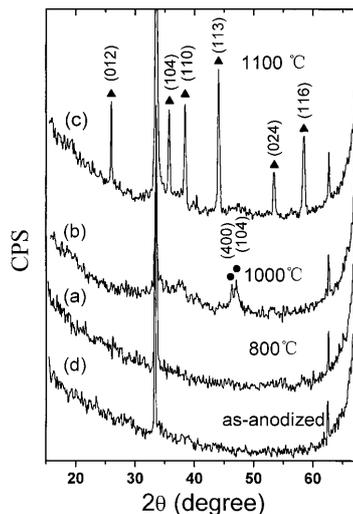


Fig. 3. XRD pattern evolution of Si-based PA films as a function of T_a in N_2 for 30 min

they are from the reflections of the (400) and (104) planes of the α - Al_2O_3 phase. Therefore, the large blueshift of the PL peaks in the sample with $T_a = 1000$ °C is closely related to the structural change of the PA film caused by high T_a . For the sample with $T_a = 1100$ °C, six new diffraction peaks, which are related to the α - Al_2O_3 phase, can be observed. This result further indicates that the appearance of the new structure in the PA films is responsible for the blueshift of the PL peaks.

According to the above XRD results, we can disclose the mechanism leading to the observed PL peaks. Obviously, the PL peaks cannot be related to alcohol groups (= Al–OH) [11] because the alcohol groups should vanish after high-temperature annealing above 500 °C. Yamamoto et al. [8] have investigated the PL band from anodic PA films formed in lower aliphatic carboxylic acids and ascribed this band to optical transitions in the colored materials incorporated with oxalate ions. If this is also the case in our experiments, we could only see one broad PL peak at 470 nm in the measured range of 300–600 nm. This spectral feature is quite different with our current experimental results. Further, these oxalate ions should have large changes under high-temperature annealing and hence the PL spectra should also have drastic changes. These changes should not be a simple blueshift in our experimental results. Ortiz et al. [12] have demonstrated a similar PL peak at 405 nm from alumina films prepared by ultrasome spray pyrolysis. The PLE spectrum of the 405-nm luminescent band was found to have two peaks at 281 and 371 nm. In our experiments, three PL peaks are observed at 263, 300, and 356 nm, and the PLE spectra of these PL peaks show three peaks at 230, 259, and 294 nm (see Fig. 4), different from the results presented by Ortiz et al. Therefore, our PL bands may not be attributed to radiative recombination from excess aluminum ions in the samples [12].

In the crystalline Al_2O_3 phase, optical transitions in a variety of defect centers (F_2 , F_2^+ , F_2^{2+} , F, and F^+) related to oxygen vacancies can show optical absorption bands and corresponding luminescence bands in the ultraviolet or violet [13, 14]. For those luminescence bands from F_2 , F_2^+ , and F_2^{2+} centers, an obvious feature is that the PL peak intensities and positions change with increasing ultraviolet illumination

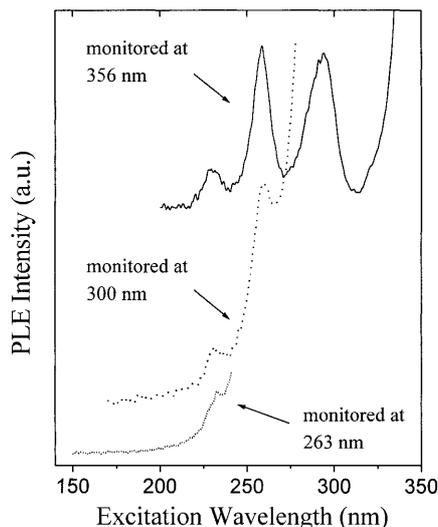


Fig. 4. PLE spectra of Si-based PA film annealed at 800 °C in N₂ for 30 min

time, because these defect centers could be ionized under illumination of an ultraviolet light to transfer each other [13, 14]. However, the PL bands obtained in our experiments hardly change in intensity and position with the illumination time. For the F center, it should have a strong PLE band at 207 (6.05 eV) nm [14], but in our result the 207 nm PLE band is rather weak. Therefore, we can also reject the F center as having an insignificant effect on the observed PL bands. A possible origin of the observed PL can be presented based on our experimental results. In Fig. 3(c) we see that the sample annealed at 1100 °C shows a perfect α -Al₂O₃ phase. In this α -Al₂O₃ phase, a luminescent center, F⁺ (oxygen vacancies with one electron), has been found to have an emission at 326 nm [15]. Its PLE spectra show three peaks at 207, 230, and 258 nm, corresponding to 1A–2B, 1A–2A, 1A–1B transitions of the F⁺ center, respectively. Since the 230 and 258 nm PLE peaks are almost equal to the values obtained in our samples and the 207 nm peak is also weakly observed in our as-anodized sample, we believe that the observed PL peaks are intimately associated with the F⁺ centers in our anodic PA films. The F⁺ center has the same local environment as that in crystalline Al₂O₃ and therefore has the same energy levels of excitation states. However, in the sample annealed at 1000 °C, the PA film displays a α -Al₂O₃ phase, and thus the local environments of the F⁺ centers have been changed. This leads to the F⁺ centers in the α -Al₂O₃ phase having different emission energies, as observed in our experiments. For the as-anodized sample and the sample annealed at 800 °C, since they do not show any structural features, the local environment of the F⁺ centers should be completely different from those in the samples annealed at 1000 and 1100 °C and thus the emission energies can be expected to have large changes. This is in agreement with our experimented results. As for the reduction of the PL intensities in the samples annealed in air, it is mainly due to the reduction of the density of oxygen vacancies. The existence of oxygen in the annealing atmo-

sphere does not change the local structures of the F⁺ center but its density. Therefore, the PL peak positions remain unchanged, whereas the PL intensities are abruptly reduced. The existence of the F⁺ center has been observed in anodic PA films on bulk Al by anodization [9]. Our experimental results further disclose the optical properties of the F⁺ center and so will be beneficial to understanding the F⁺ center structure.

The formation of the F⁺ center in our samples is understandable. So far, the commonly accepted theory is that the pore development of anodic PA films is a result of competition between alumina growth at the oxide/metal interface and oxide dissolution at the oxide/electrolyte interface [16]. The dominant model of the charge transport is ionic conduction across the barrier alumina in a high electric field (1×10^7 V cm⁻¹) [17]. Oxygen ions migrate through the barrier by a vacancy mechanism [18] and hence partial oxygen vacancies should remain in the formed anodic PA films. After an electron is trapped by an oxygen vacancy, a F⁺ center is formed.

In summary, we have investigated the light-emission properties of Si-based anodic PA films as light sources. Two strong ultraviolet peaks and one violet PL peak were observed for the as-anodized sample and those annealed under different temperatures. Based on the structural analysis and discussions of the thermal annealing behaviors of the PL and PL excitation spectra, we suggest that the oxygen-related defect center, F⁺, may be responsible for the observed PL peaks.

Acknowledgements. This work was supported by the National Natural Science Foundation of China (Grant Nos. 59832100 and 60076007).

References

1. D. Al-Mawlawi, N. Coombs, M. Moskovits: *J. Appl. Phys.* **70**, 4421 (1991)
2. C.A. Huber, T.E. Huber, M. Sadoqi, J.A. Lubin, S. Manalis, C.B. Prater: *Science* **263**, 800 (1994)
3. D. Al-Mawlawi, C.Z. Liu, M. Moskovits: *J. Mater. Res.* **9**, 1014 (1994)
4. H. Masuda, K. Fukuda: *Science* **268**, 1466 (1995)
5. P. Hoyer, N. Baba, H. Masuda: *Appl. Phys. Lett.* **66**, 2700 (1995)
6. Z.B. Zhang, J.Y. Ying, M.S. Dresselhaus: *J. Mater. Res.* **13**, 1745 (1998)
7. S.L. Sung, S.H. Tsai, C.H. Tseng, F.K. Chiang, X.W. Liu, H.C. Shih: *Appl. Phys. Lett.* **74**, 197 (1999)
8. Y. Yamamoto, N. Baba, S. Tajima: *Nature* **289**, 572 (1981)
9. Y. Du, W.L. Cai, C.M. Mo, J. Chen, L.D. Zhang, X.G. Zhu: *Appl. Phys. Lett.* **74**, 2951 (1999)
10. J.H. Wu, J.P. Zou, Q. Zhu, X.M. Bao: *Chin. J. Semicond.* **20**, 318 (1999)
11. M. Ruckschloss, T. Wirschem, H. Tamura, G. Ruhl, J. Oswald, S. Veprek: *J. Lumin.* **63**, 279 (1995)
12. V. Ortiz, J.C. Alonso, V. Pankov, D. Albarran: *J. Lumin.* **81**, 45 (1999)
13. A. Al Ghamdi, P. Townsend: *Nucl. Instrum. Methods Phys. Res., Sect. B* **46**, 133 (1990)
14. G.J. Pogatshnik, Y. Chen, B.D. Evans: *IEEE Trans. Nucl. Sci.* **NS-34**, 1709 (1987)
15. D. Evans, M. Stapelbroek: *Phys. Rev. B* **18**, 7089 (1978)
16. J.P. O'Sullivan, G.C. Wood: *Proc. R. Soc. London, Ser. A* **317**, 511 (1970)
17. J.W. Diggle, T.C. Downie, C.W. Goulding: *Chem. Rev.* **69**, 365 (1969)
18. J. Siejka, C. Ortega: *J. Electrochem. Soc.* **124**, 883 (1977)