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Characterization of the anomalous luminescence properties from self-ordered porous anodic alumina with oxalic acid electrolytes

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ABSTRACT

The pore height and diameter of the nanoscale structure of porous anodic alumina (PAA) film produced by the anodization technique are controllable. The structures can be applied for the fabrication of visible spectral range optical devices. In this study we characterized the luminescence properties of self-ordered PAA films evaporated onto silicon substrates. Anomalous luminescence properties produced by carrier confinement were observed in PAA films fabricated with the introduction of oxalic acid electrolytes during the anodization process. The recombination mechanisms were characterized by measuring the temperature-dependent photoluminescence (PL) spectra. The PL spectra of PAA films show an asymmetrical luminescence profile in the blue emission region. The Gaussian function divides these into two subbands. The subbands originate from two different kinds of oxygen-deficient defect centers, namely, F^+ (oxygen vacancy with only one electron) and F (oxygen vacancy with two electrons) centers. The F centers are densest at the surface but show a gradual decrease with an increase in the pore wall depth and electrolyte concentration. However, the reverse trend is observed for the F^+ centers. In strong contrast to the commonly expected trend of a uniform reduction in non-radiative recombination with decreasing lattice temperature, we observed an anomalous low-temperature PL growth and decline between the F and F^+ centers. Theoretical models corroborate the anomalous temperature behavior. All the calculations are in agreement with the experimental observations.

1. Introduction

In recent years, self-ordered porous anodic alumina (PAA) film has been extensively used as template, mask, or host materials for the synthesis of various nanostructures, and building blocks for developing nanoscale devices. Recently, the study of self-ordered PAA films has been developing rapidly leading to notable achievements. Self-ordered PAA films have become widely accepted for applications in the field of electronic materials [1–9]. It is known that a carefully controlled anode of aluminum in an acidic electrolyte produces a thin layer of dense aluminum oxide, followed by an ordered array of nanopores [10]. The advantages of porous anodic alumina include self-assembly, high aspect ratio, uniform pore size, uniform channel length and easy fabrication.

However, the origin of the observed blue emission band is still not clear. Du et al. and Li et al. have attributed the blue emission band to the presence of singly ionized oxygen vacancies (F^+ centers) [11,12]. According to Xu et al. the oxalic impurities can be transformed into luminescent centers [13]. Huang et al. noted two different kinds of oxygen-deficient defect centers: F (oxygen vacancies with two electrons) and F^+ (oxygen vacancies with only one electron) centers [14].

In this study, we investigated the temperature dependence of the PL spectra of self-ordered PAA membranes fabricated with different oxalic acid concentrations. The temperature-dependent photoluminescence (PL) spectra were measured to characterize the recombination mechanisms. The effect of oxalic ions on the PL properties of PAA was investigated in-depth, and the mechanism was also discussed.

2. Experiments

In this work, we used (100)-oriented p-type silicon wafer substrates. A high purity aluminum slug (99.999%, 3 mm dia × 6 mm L spec, Guv Team) was used as the target material. Aluminum layers with a thickness of about 2 μm were deposited onto silicon substrates using the thermal evaporation technique. The vacuum chamber was maintained at a pressure of 2.6×10^{-6} Pa. Before deposition, the

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silicon wafers were rinsed in acetone and isopropyl alcohol (IPA) for degreasing and then etched in a hydrofluoric acid (HF) solution for 1 min to remove oxide impurities. This was followed by further rinsing of the wafer in deionized water. After deposition, the aluminum layers were annealed at 400 °C in N_2 for 3 h to improve the homogeneity of the sample. Annealing also improves the bonding of the aluminum/silicon interface and reduces the interfacial resistivity which directly affects the anodic process.

Anodization was carried out in oxalic acid (from 0.1 M to 0.5 M). A graphite plate was used as a cathode. The temperature was kept at 3 °C under a constant current density of 5 mA/cm^2. Ordered nanopore arrays were obtained using a two-step anodizing process. Si-base aluminum was anodized for 10 min. The pre-formed alumina was removed by phosphoric acid and then anodized for 22 min. Finally, the sample was immersed in 30 wt.% phosphoric acid for 25 min to widen the holes in the PAA membranes. Samples were then rinsed thoroughly in deionized water and dried in N_2 gas. Field-emission scanning electron microscopic (FE-SEM) images of the sample surfaces were obtained from the Formosa Plastics Group. For temperature-dependent photoluminescence (PL) measurements samples were mounted in a closed-cycle He cryostat and excited by a continuous-wave He–Cd laser, while gradually increasing the temperature from 20 to 300 K. The average excitation intensity was 20 mW. The luminescence signal was dispersed through a 0.5-m monochromator and later detected by a Si photodiode. A standard lock-in amplification technique was employed.

3. Results and discussion

The surface morphology of the anodic alumina film layer grown in 0.1 M oxalic acid electrolytes has a fairly regular nano-porous structure as can be clearly seen in Fig. 1. The average diameter of the PAA nanopores is about 40 nm with an interpore distance of approximately 60 nm.

The unique correlation between the structural characteristics and carrier transport of the PAA film is elucidated with the addition of oxalic acid electrolytes (from 0.1 M to 0.5 M). It is of interest to examine the radiative recombination of the confined electrons and holes at low temperature. Fig. 2 shows the photoluminescence spectra of PAA films with oxalic acid electrolytes at: (a) 0.1 M, (b) 0.2 M, (c) 0.3 M, (d) 0.4 M and (e) 0.5 M, measured temperature of about 20 K, and injected with a current density of 5 mA/cm^2. Past studies have concentrated on the optical properties of self-ordered porous anodic alumina membranes. Previous investigations have observed anomalous blue PL luminescence from the PAA membranes on aluminum foils. The PL spectra of PAA films have an asymmetrical luminescence profile in the blue emission region. There are two clearly observable blue emission bands in the photoluminescence spectra of the PAA membranes in the range of 2.2 to 3.2 eV. The PL results can be divided into two bands. The variation in the anomalous PL luminescence is caused by optical transitions which originate from two different kinds of oxygen-deficient defect centers, the F$^+$ and F defect centers, which exist in PAA membranes. The high-energy band, the so-called F$^+$ center, is known to originate from oxygen vacancies with a trapped electron, and the low-energy band, the so-called F center, originates from oxygen vacancies with two trapped electrons. The density of the F centers is the largest at the surface, gradually decreasing with an increase in electrolyte concentration. The PL spectra show the gradual reduction and increase in the overall PL intensity brought about by increasing the oxalic acid concentration. However, the reverse trend is observed for the F$^+$ centers.

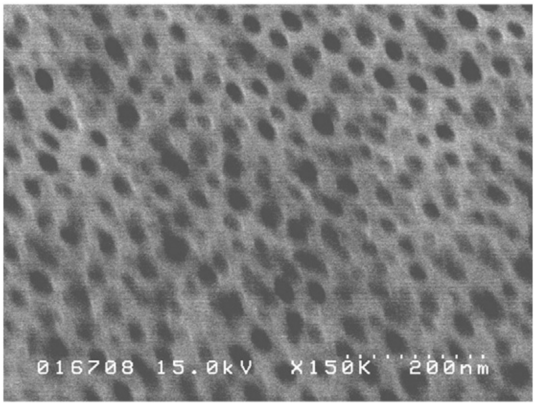

Fig. 1. FE-SEM — surface morphology image of the porous anodic alumina grown in 0.1 M oxalic acid electrolytes.

We also examine the competition in the carrier transport between the F$^+$ transition and F transition centers. The normalized PL intensity ratio of F transitions to F$^+$ transitions is plotted as a function of oxalic acid concentration for the PAA film with oxalic acid electrolytes in Fig. 3. The anomalous low-temperature PL growth and decline observed between the F and F$^+$ centers is in strong contrast to the commonly expected trend of uniform reduction of non-radiative recombination with decreasing lattice temperature. The current density used during anodizing of the samples was the same (5 mA/cm^2) and anodizing time was also the same (22 min). The sample was immersed in 30 wt.% phosphoric acid for 25 min to widen the holes in the PAA membranes. With increasing the concentrations of electrolyte, the resistivity of the electrolyte and the voltage across the PAA film both were increased simultaneously [15]. It means that widening of the pores may take place with the increase in concentration of electrolyte. Furthermore, it is found that homogeneity of 0.4 and 0.5 M oxalic acid electrolyte would vary at 3 °C because of the formation of a deposit in highly concentrated electrolyte. When the oxalic acid concentration is slightly increased over 0.1 M, the ratio of F transitions to F$^+$ transitions rises efficiently reaching a maximum at about 0.4 M. After further increasing the concentration to 0.5 M, the PAA film exhibits a larger reduction in this ratio.

The scattering processes are taken into account to formulate a rate equation model which corroborates the unique thermal behaviors and describes the carrier trapping and detrapping processes in the quantum-sized heterostructure. As a result, the thermally related abatement of the cross-section is sufficiently damaging to augment the radiative recombination in the PAA films over a broad temperature range. However, as far as the quantum efficiency at a constant temperature is concerned, the optical characteristics exhibited by the higher concentration PAA films are poorer than those exhibited by the lower concentration films, as expected. Notwithstanding this, a well-constructed PAA heterostructure, with a high fraction of captured cross-sections can ameliorate the performance of blue emissions in PAA films. The exciton wavefunction can be successfully tailored by a nanostructure which facilitates the localization of the injected carriers and promotes radiative recombination in the radiative recombination region of the PAA films. Inferentially, the higher the confinement ability of energetic excitons, the larger the cross-sections for impinging carriers, which inhibits the radiative recombination in the F center region and effectively increases the recombination intensity in the F$^+$ center region.

Fig. 4 shows an Arrhenius plot of the integrated PL intensity of the color centers for the: (a) F$^+$ transitions and (b) F transitions for the porous anodic alumina with oxalic acid electrolytes over a broad temperature range. The quenching of the PL luminescence with temperature is attributed to the thermal emission of carriers that have escaped from the oxygen-deficient defect centers caused by alloy disordering and interface fluctuations. Thus the activation energy is correlated with the exciton confinement ability. The following expression is generally used for calculating activation energy in thermally activated processes [16]:

$$I(T) = \frac{I_0}{1 + Se^{(-E/k_B T)}}, \qquad (1)$$

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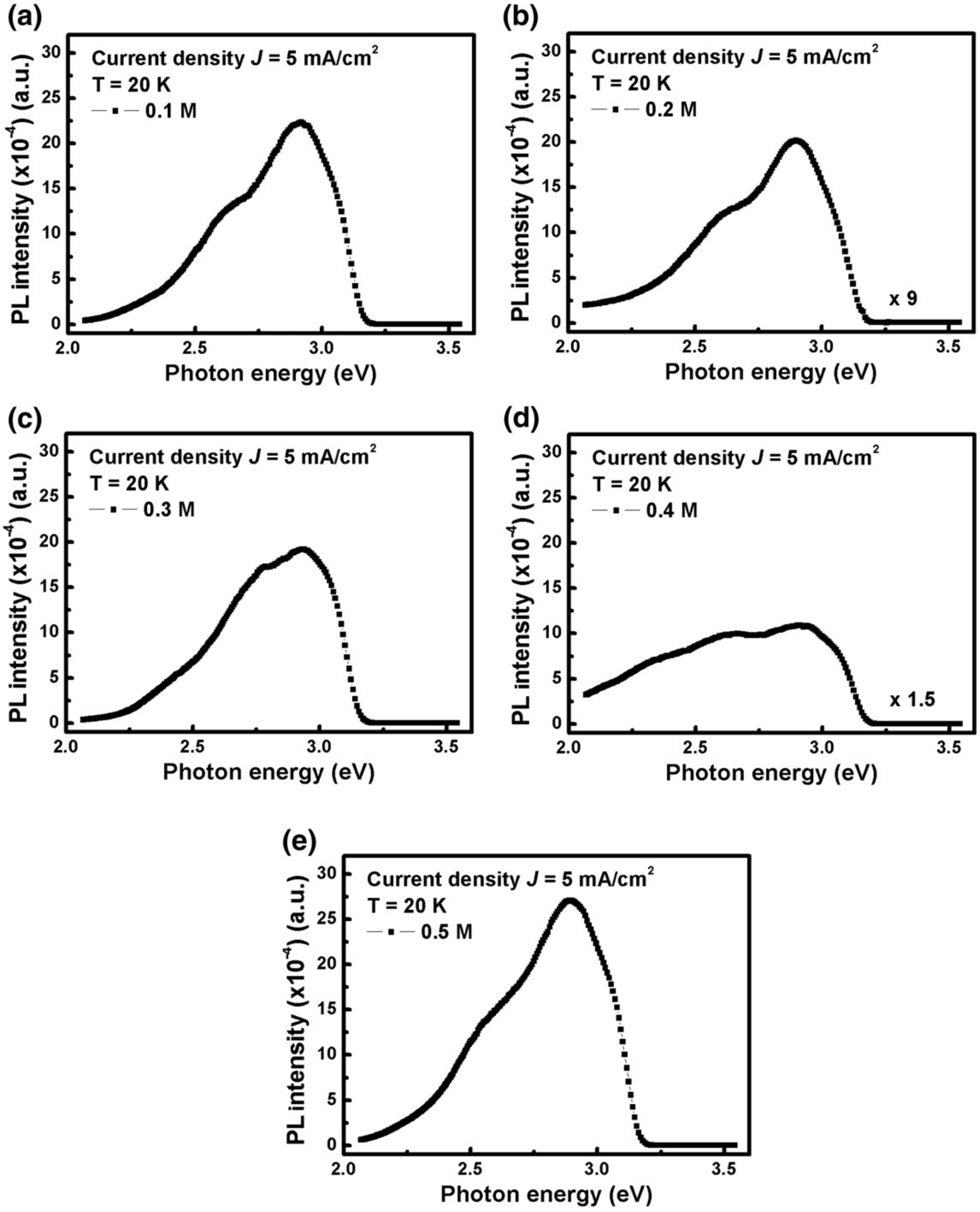

Fig. 2. Photoluminescence spectra of the porous anodic alumina with oxalic acid electrolytes of: (a) 0.1 M, (b) 0.2 M, (c) 0.3 M, (d) 0.4 M, and (e) 0.5 M, measured using a continuous-wave He–Cd laser with wavelength of 325 nm as the exciting source.

where $I(T)$ is the temperature-dependent integrated PL intensity; I_0 is the integrated PL intensity at 0 K; E is the activation energy; k_B is the Boltzmann's constant; and S is the rate constant. The activation energies E of the F^+ transitions in the PAA film with oxalic acid electrolytes from 0.1 M to 0.5 M extracted from the low-excitation Arrhenius are 165, 136, 116, 75, and 190 meV, respectively. On the other hand, the activation energies E of the F transitions of the PAA film with oxalic acid electrolytes from 0.1 M to 0.5 M extracted from the low-excitation Arrhenius are 139, 110, 92, 60, and 156 meV, respectively. The activation energy is related to the activation energies of the captured cross-sections of the non-radiative recombination centers. The experimental results demonstrate that a higher concentration has a less carrier confinement that can decrease the radiative recombination rate. Furthermore, the integrated intensity of the F^+ transition in PAA film structures is larger than that of the F transitions and this can markedly suppress carrier leakage and increase photoexcited carrier density. The anomalous growth and decline of low-temperature PL between the F and F^+ centers is in strong contrast to the commonly expected trend of a uniform reduction in the non-radiative recombination with decreasing lattice temperature.

4. Conclusions

In this study we have investigated the unique correlations between the structural characteristics and carrier transport of PAA film with oxalic acid electrolytes from 0.1 M to 0.5 M over a broad range of temperatures. The PL spectra of the PAA films show an asymmetrical luminescence profile in the blue emission region. The Gaussian function

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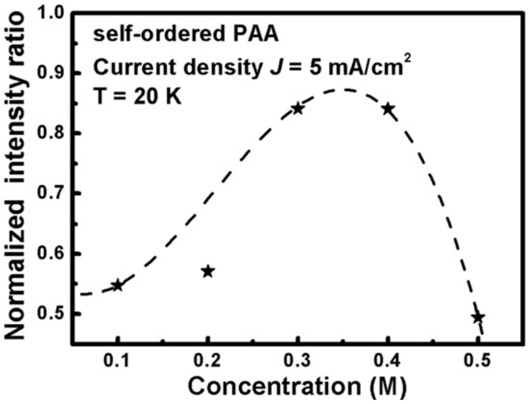

Fig. 3. Normalized PL intensity ratio of F to F$^+$ transitions plotted as a function of oxalic acid concentration for the porous anodic alumina with oxalic acid electrolytes.

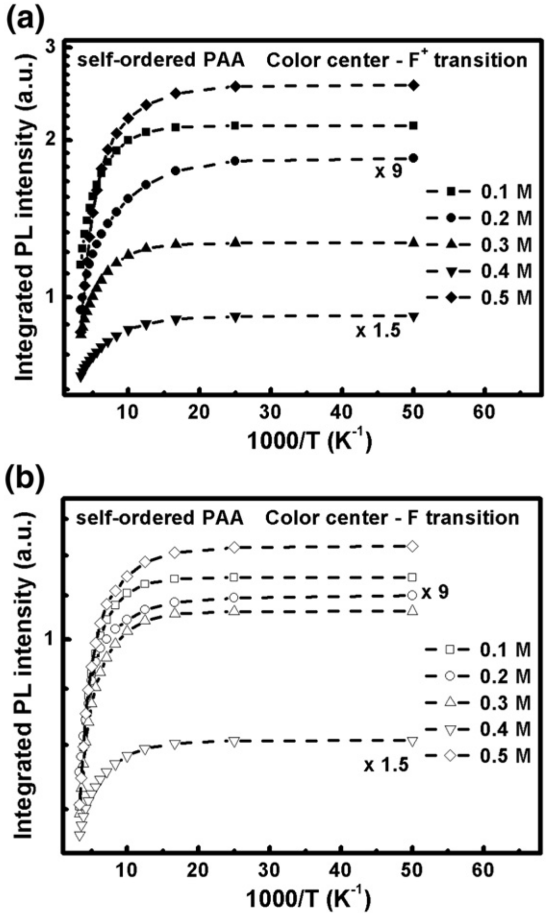

Fig. 4. Arrhenius plot of the integrated PL intensity of color centers for: (a) F$^+$ transitions; and (b) F transitions in porous anodic alumina with oxalic acid electrolytes.

divides this into two subbands which originate from the two kinds of different oxygen-deficient defect centers, the F$^+$ and F centers. When the oxalic acid concentration is slightly increased from 0.1 M, the ratio of the F transitions to F$^+$ transitions rises until reaching a maximum at about 0.4 M. With a further increase in the concentration up to 0.5 M, it is found that the PAA film exhibits a larger reduction in ratio. In strong contrast to the commonly expected trend of a uniform reduction in non-radiative recombination centers with decreasing lattice temperature, we observe an anomalous low-temperature PL growth and decline between the F and F$^+$ centers. Both the carrier transport mechanism and the abnormal intensity evolution as a function of temperature are found to be in good agreement with the theoretical model.

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References

[1] K.-H. Jung, J.-W. Yoon, N. Koshizaki, Y.-S. Kwon, Jpn. J. Appl. Phys. 44 (2005) 5300.
[2] C.-J. Yang, S.-M. Wang, S.-W. Liang, Y.-H. Chang, C. Chen, J.-M. Shieh, Appl. Phys. Lett. 90 (2007) 033104.
[3] G.D. Sulka, S. Stroobants, V. Moshchalkov, G. Borghs, J.-P. Celis, J. Electrochem. Soc. 149 (2002) D97.
[4] J.H. Chen, C.P. Huang, C.G. Chao, T.M. Chen, Appl. Phys., A 84 (2006) 297.
[5] T. Gao, G. Meng, L. Zhang, J. Phys, Condems. Matter 15 (2003) 2071.
[6] J. Hohlbein, U. Rehn, R.B. Wehrspohn, Phys. Status Solidi, A 201 (2004) 806.
[7] K. Huang, L. Pu, Y. Shi, P. Han, R. Zhang, Y.D. Zheng, Appl. Phys. Lett. 89 (2006) 201118.
[8] Z. Li, K. Huang, J. Phys, Condems. Matter 19 (2007) 216203.
[9] Y. Li, G.H. Li, G.W. Meng, L.D. Zhang, F. Phillipp, J. Phys, Condems. Matter 13 (2001) 2691.
[10] J.S. Lee, G.H. Gu, H. Kim, K.S. Jeong, J. Bae, J.S. Suh, Chem. Mater. 13 (2001) 2387.
[11] Y. Du, W.L. Cai, C.M. Mo, J. Chen, L.D. Zhang, X.G. Zhu, Appl. Phys. Lett. 74 (1999) 2951.
[12] Y. Li, G.W. Meng, L.D. Zhang, F. Phillipp, Appl. Phys. Lett. 76 (2000) 2011.
[13] W.L. Xu, M.J. Zheng, S. Wu, W.Z. Shen, Appl. Phys. Lett. 85 (2004) 4364.
[14] G.S. Huang, X.L. Wu, Y.F. Mei, X.F. Shao, J. Appl. Phys. 93 (2003) 582.
[15] H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, T. Tamamura, Appl. Phys. Lett. 71 (1997) 2770.
[16] M. Hao, J. Zhang, X.H. Zhang, S. Chua, Appl. Phys. Lett. 81 (2002) 5129.

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