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Abstract
Strong photoluminescence bands range from 300 to 600 nm at room temperature have been observed in anodic alumina membranes (AAM). It was found that the photoluminescence (PL) intensity and peak position of AAM depend strongly on the excitation wavelength, and the PL intensity of AAM prepared in $C_2H_2O_4$ is much higher than for AAM prepared in H_2SO_4. There are two peaks in the PL bands; one is at constant wavelength of 460 nm, and the other increases almost linearly from 420 to 465 nm with excitation wavelength for AAM prepared in $C_2H_2O_4$ and from 360 to 465 nm for AAM prepared in H_2SO_4. Annealing treatment of the as-prepared AAM results in an apparent reduction of the intensity of the blue emission at shorter excitation wavelength, while at longer excitation wavelength (longer than 320 nm) the PL intensity firstly increases, and at 500 °C reaches a maximum value, then decreases. It is considered that there are two PL centres; one originates from the oxygen-related defects in the barrier layer, and the other is correlated with the aluminum incorporated into the anion-contaminated alumina layer in the AAM.

1. Introduction

Anodic alumina membranes (AAM) are easily available by controlled anodization of aluminum surfaces in aqueous acids. Their properties, such as optical transparency, temperature stability, and pores of variable widths and lengths, make them unique templates for xerogel solids doped with luminescent lanthanide ions [1–3]. Titania xerogel was shown to be a good host for optically active Tb [2], Er [3, 4] and Eu [5] trivalent ions. Sol–gel synthesis of titania xerogel in the pores of anodic alumina may produce regular periodical structures that possess strong visible luminescence [6].

As a template for synthesizing new luminescence materials, the study of the luminescence of AAM itself is very important in investigating the mechanisms of new properties, because the properties of the AAM certainly affect the properties of materials based on AAM. Du and co-workers [7] studied the photoluminescence (PL) of AAM prepared in $C_2H_2O_4$ or H_2SO_4 and found a blue PL band in the wavelength range of 400–600 nm. Schmid found that the PL of AAM depends on the preparing conditions and can be eliminated by thermal decomposition at 900 °C before filling [8]. Recently Gao [9] studied the role of impurity in the PL of AAM prepared in $C_2H_2O_4$, and attributed the PL peak at 470 nm to oxalic impurities. It is shown in this paper, however, that the PL property of AAM is very complex, and there is a significant excitation wavelength dependence of the PL band over a wide range of excitation energies; the PL peak position and intensity depend not only on the excitation wavelength, but on the pore size as well.

In our previous study, the optical absorption spectra of AAM were reported [10]; in this paper the wavelength dependent PL properties of AAM are reported and the influence of annealing treatment is discussed.

2. Experimental details

AAM templates were prepared by a two-step anodization process. Briefly, high-purity (99.999%) aluminum foils were used as the starting material. Prior to anodizing, the aluminum was annealed at 500 °C in order to obtain homogeneous conditions for pore growth over large areas. Then aluminum foils were electropolished at 23 V in a mixture of 70% perchloric acid and ethanol (1:9) at 4 °C for 2 min. Anodization was carried out either at 40 V DC in 0.25 M aqueous oxalic acid electrolyte at 7 °C (40 nm AAM) or at 15–27 V in a 0.3 M sulfuric acid solution at 0 °C for several hours (30 nm AAM). The formed alumina was then removed by a mixture of phosphoric acid and chromic acid, and the Al sheet was anodized again under the same conditions as those in the first treatment for 8–20 h. After the anodization, the central substrate was removed in a saturated $SnCl_4$ solution, then the barrier was dissolved in 6 wt% phosphoric acid solution at 30 °C for 60 min; finally, the AAMs were dried at 80 °C for 1 h. Heat treatment was carried out at 300, 500, 700 and 900 °C for 1 h in air. PL spectra were measured in an Edinburgh FLS 920 spectrophotometer with an Xe lamp as the excitation light source.

3. Results and discussion

Figure 1 shows emission and the corresponding excitation spectra of the as-prepared AAMs with pore size of 40 nm prepared in $C_2H_2O_4$ (denoted as AAM_O). There is a wide blue PL band in the wavelength range of 340–600 nm, figure 1(a), and the peak intensity of the PL band firstly increases with the increase of the excitation wavelength, and at 320 nm reaches a maximum value, which is nearly ten times larger than that at 265 nm, then decreases. The maximum peak position of the emission band is at constant wavelength, i.e. 433 nm, when excited at wavelengths ranging from 265 to 320 nm, and then moves to longer wavelength; see the inset in figure 1(a). The corresponding excitation spectra are also very widely spread, from 225 to 450 nm (see figure 1(b)), and the maximum peak intensity of the excitation band firstly increases with the increase of the emission wavelength, and at 440 nm reaches a maximum value, which is nearly ten times larger than that at 360 nm, then decreases. The peak position of the excitation spectra moves to longer wavelength with the increase of emission wavelength; see the inset in figure 1(b).
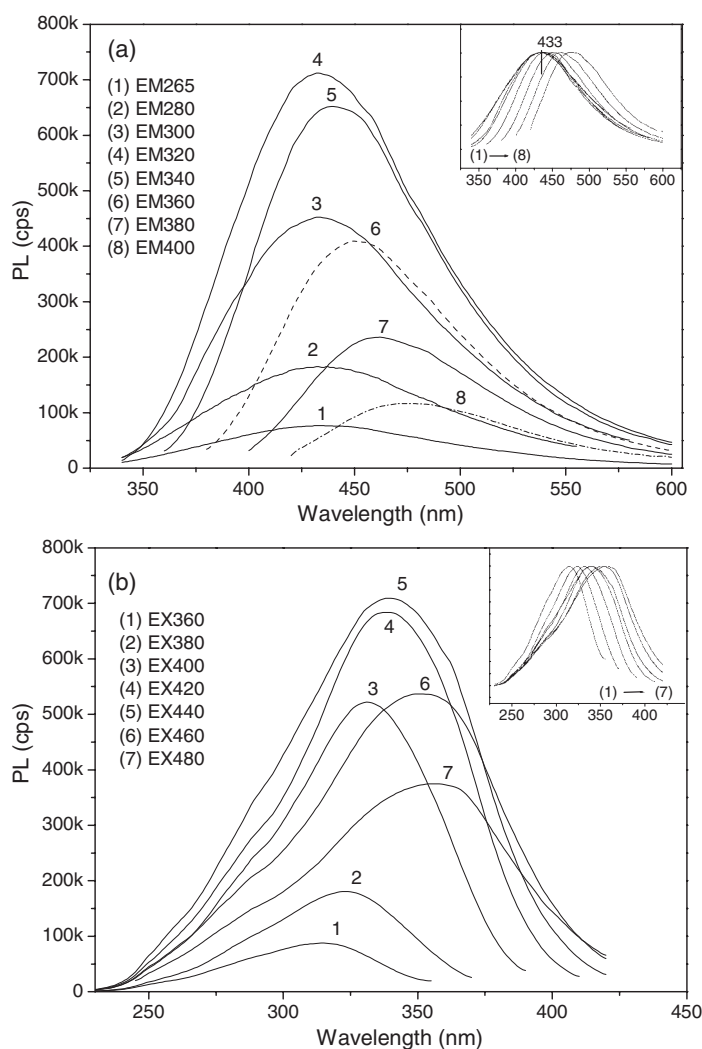
Figure 1. (a) Emission and (b) excitation spectra of AAM with pore size of 40 nm prepared in $C_2H_2O_4$. The insets show the normalized spectra.

All the obtained spectra can be decomposed in several Gaussian distributions, and it was found that deconvolution with a minimum of two components reproduced the spectra without deviations, as shown in figure 2. From figure 2(a) one can see that for emission spectra one Gaussian fit peak is at constant wavelength of 460 nm and the other increases almost linearly from 420 to 465 nm with the increase of excitation wavelength, while for excitation spectra, figure 2(b), one Gaussian fit peak is at constant wavelength of 280 nm and the other also shifts to longer wavelength along with the wavelength of emission. These results suggest that there might exist two mechanisms for the PL, and the PL spectra depend strongly on the excitation wavelength.

After annealing treatment it was found that the peak intensity of the PL band decreases with temperature when excited at wavelengths less than 320 nm (see figures 3(a) and (c)), and increases with temperature when excited at wavelengths longer than 320 nm. The PL intensity
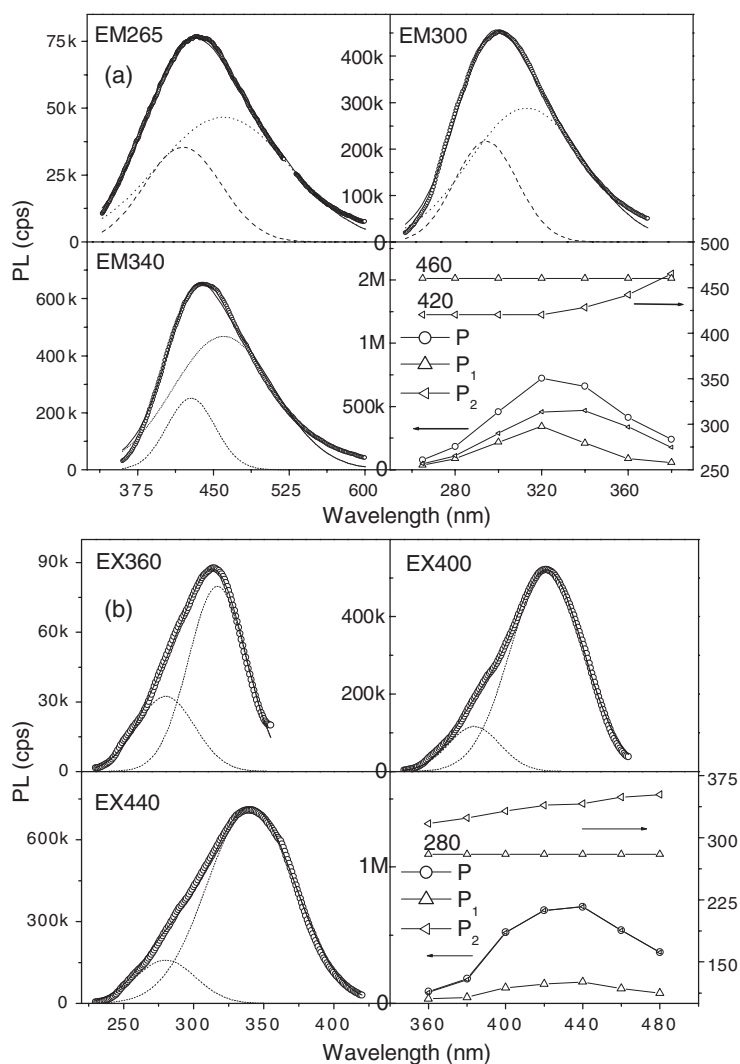
Figure 2. The Gaussian fitting of excitation (a) and emission (b) spectra together with the changes of Gaussian fitting peak position and PL intensity with wavelength. (AAM_O).

reaches a maximum value at 500 °C and then decreases; see figures 3(b) and (c). Even after annealing treatment at 900 °C, the PL intensity is still very strong, as shown in figure 3(d). It is worth noting that the first PL peak intensity increases with excitation wavelength at the same annealing temperatures, as can be clearly seen in figure 3(d). The Gaussian fittings of emission and excitation spectra after annealing treatment give similar results to those without annealing.

Figure 4 shows the PL spectra of the as-prepared AAM with pore size of 30 nm prepared in H_2SO_4 (denoted as AAM_S). The PL intensity and peak position of emission and excitation spectra also change with excitation and emission wavelength, respectively, and the maximum intensity of the PL band, at a wavelength of 360 nm, is only four times larger than that at 265 nm. There are obviously two peaks for both emission and excitation spectra, which is
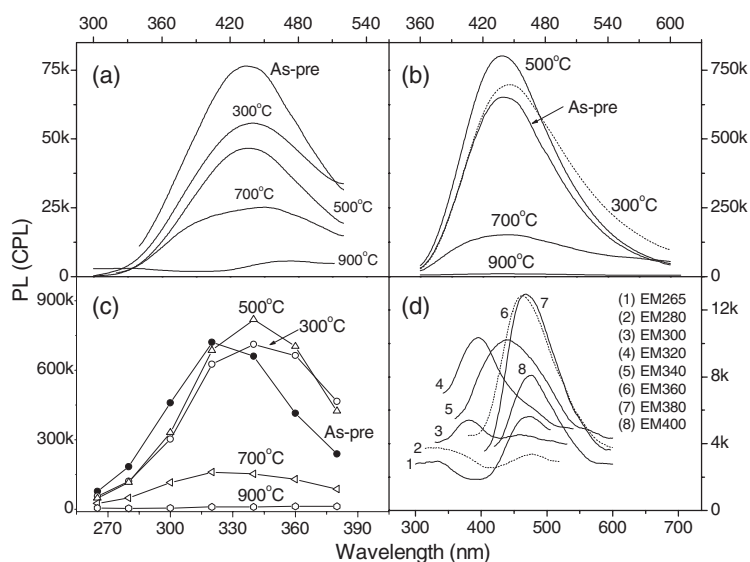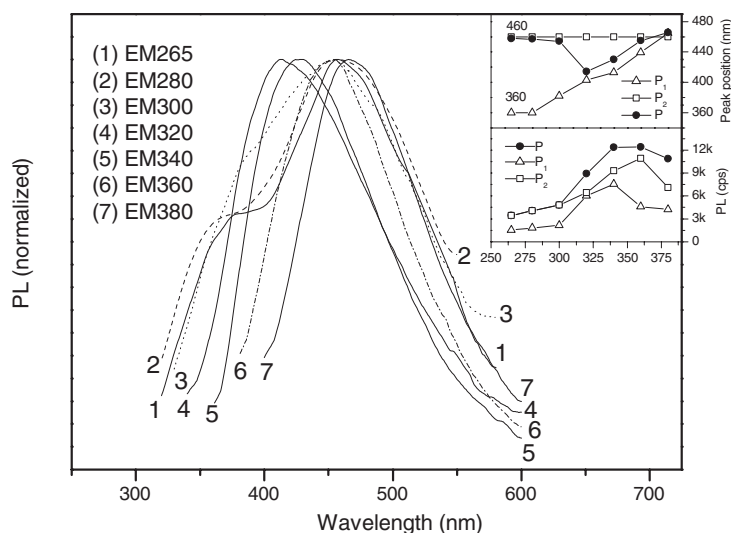
Figure 3. PL spectra of AAM_O annealed at different temperatures: (a) excited at 265 nm, (b) excited at 340 nm, (c) maximum PL intensity at different excitation wavelengths and (d) heat-treated at 900 °C.
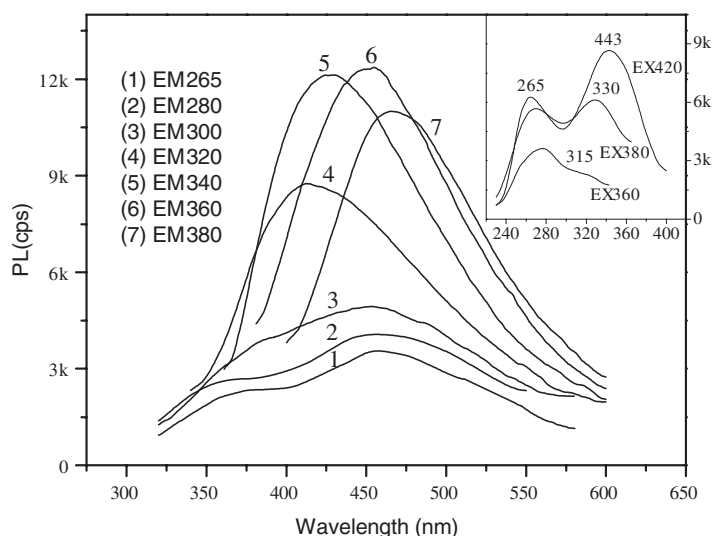

Figure 4. PL spectra of AAM with pore size of 30 nm prepared in H_2SO_4 excited with different wavelengths. The inset shows the corresponding excitation spectra.

different from AAM prepared in $C_2H_2O_4$. The main peak position of the PL band firstly moves to shorter wavelength and then moves to longer wavelength (see figure 5), which might be due to the fast increase in the intensity of the PL peak at short wavelength, as shown in the insets in figure 5. The Gaussian fitting of emission and excitation spectra also contains two components; one peak is at 460 nm (or 265 nm) and the other also increases linearly with excitation (or emission) wavelength from 365 to 460 nm. After annealing treatment it was found that the PL

Figure 5. Normalized PL spectra of AAM_S excited at different wavelengths. The upper inset is the PL peak position at the maximum intensity and two Gaussian fitting peak positions; the lower inset is the corresponding peak intensity.
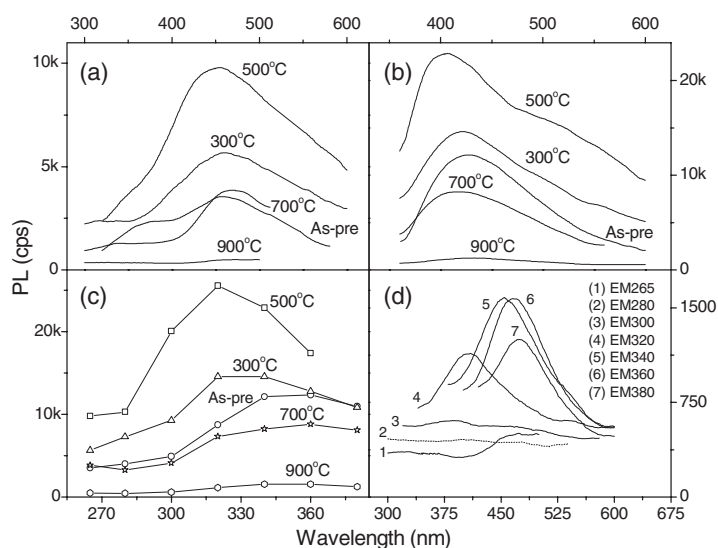
Figure 6. PL spectra of AAM_S annealed at different temperatures: (a) excited at 265 nm, (b) excited at 340 nm, (c) the maximum PL intensity at different excitation wavelengths and (d) heat-treated at 900 °C.

peak intensity firstly increases with temperature and at 500 °C reaches a maximum value, then decreases (see figure 6), which is slightly different from that of AAM prepared in $C_2H_2O_4$.

From the above results one can see that the PL intensity and peak position of AAM depend strongly on the excitation wavelength, and the PL intensity of AAM prepared in $C_2H_2O_4$ is much higher than that in H_2SO_4 (by one order of magnitude). There are clearly two components in the emission and excitation spectra, and for emission spectra, one is situated at a constant
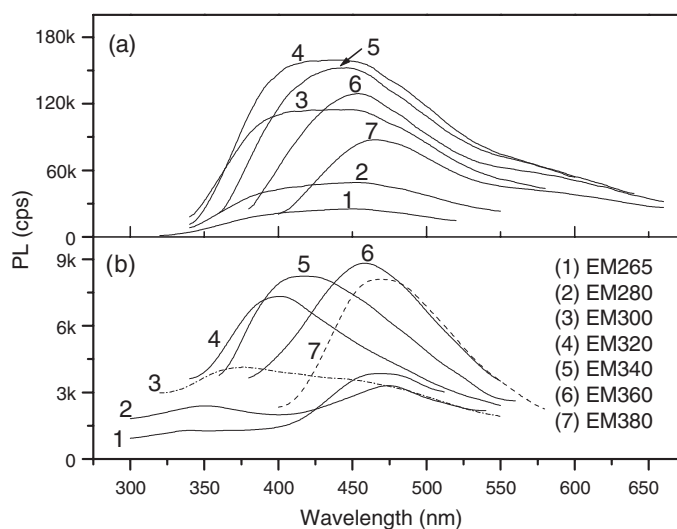
Figure 7. PL spectra excited at different wavelengths of AAM annealed at 700 °C: (a) AAM_O and (b) AAM_S.

wavelength of 460 nm, and the other increases linearly with excitation wavelength, while for excitation spectra one is situated at a constant wavelength of 265 and 280 nm for AAM_O and AAM_S, respectively, and the other also increases linearly with emission wavelength. The result indicates that the PL of AAM_O and AAM_S might have the same origin.

There are many studies concerning the PL mechanisms of AAM and alumina. Du *et al* [7] attribute the PL band to singly ionized oxygen vacancies (F^+ centres) in porous alumina membranes. Gao *et al* [9] attribute the PL peak at 470 nm of AAM prepared in $C_2H_2O_4$ to oxalic impurities. Huang suggested that the blue PL bands in AAM originate from optical transitions in two kinds of different oxygen-deficient defect centres [11]. Ishizaka and Kurokawa observed a strong luminescence of 300–500 nm for pure alumina film, and found the PL was dependent on the heat treatment temperature of the gel, and disappeared after treating at temperatures higher than 600 °C. The luminescence band was attributed to oxygen defect sites in alumina [12]. Yu also observed a strong PL band at 300–550 nm for nanocrystal α-Al_2O_3 and a PL peak at 421 nm excited with wavelength of 254 nm, and suggested that the defect level in the nanometer alumina powder should be taken into account for the mechanism of luminescent emission bands [13].

The AAM cell structure consists of three layers, pore, anion-contaminated alumina and relative pure alumina, and the barrier layer (the ratio thickness of relative pure alumina region to acid anion-contaminated material) in sulphuric acid is lower than that in oxalic acid [14]. The PL can come from both anion-contaminated alumina and relatively pure alumina, which indicates that there might exist two PL centres. Our results clearly indicate that there are two peaks in both the emission and excitation spectra of AAM: one is at constant wavelength and the other shifts to longer wavelength with the wavelength of excitation or emission. From these results it could be implied that the PL peak at constant wavelength, i.e. 460 nm, might be related to the relatively pure alumina in AAM, and the other correlated with the anion-contaminated alumina. The fact that the first PL peak intensity increases with excitation wavelength at the same annealing temperatures (see figures 3, 6 and 7) indicates that the contribution to PL band coming from the first peak (that is the component changes with excitation) increases. This result clearly indicates that there are two PL centres in AAM.

It has been found that during the fabrication of AAM, some aluminum might incorporated into the barrier layer [7] forming anion-contaminated alumina, and when a metallic ion is placed into a glass matrix, the ions surrounding the ion influence its energy levels giving place to the splitting of the levels into several components which are shifted and broadened [15]. This might be responsible for changes of the PL peak position with excitation wavelength.

Since the PL intensity of AAM firstly increases with annealing temperature, and at $500\,°C$ reaches a maximum value, then decreases, one might deduce that the PL is related to the oxygen vacancies both in pure and anion-contaminated alumina in AAM, instead of oxalic or sulfite impurities. It is well known that in the production of AAM, electrolyte ions are incorporated within the structure as impurities [16], such as $C_2O_4^{2-}$ and $HC_2O_4^{-}$ ions in $C_2H_2O_4$, which are converted to molecular CO_2 and CO_3^{2-} ions upon annealing treatment [17]. The oxalic or sulfite impurities might serve as PL annihilation centres instead of PL emission centres, and annealing treatment can remove these annihilation centres. The aluminum incorporated into the barrier layer is oxidized under an oxygen-poor atmosphere, and it is possible that in the newly formed alumina there exist many oxygen centres [10]. Both of the above factors will increase the PL intensity. With a further increase in the annealing temperature the concentration of oxygen vacancies decreases along with the corresponding PL intensity [7].

Why the PL intensity of AAM prepared in $C_2H_2O_4$ is much stronger than that of AAM prepared in H_2SO_4 is currently unclear; it is believed to result from many absorption states or various kinds of defects existing in the AAM prepared in $C_2H_2O_4$ owing to the large pore size and the high thickness of the relatively pure alumina layer [14]. Therefore, the probability of the transition between energy levels in the AAM prepared in $C_2H_2O_4$ can be greatly enhanced as a result of their interaction in such material. In fact it has been found that the PL band of AAM also depends on the pore size, and the full width at half maximum of the PL band of AAM prepared in H_2SO_4 increases linearly with decreasing pore size; this has been observed experimentally and will be reported elsewhere [18].

4. Conclusions

AAM prepared in $C_2H_2O_4$ and H_2SO_4 show a strong PL band ranging from 300 to 600 nm at room temperature. The PL intensity of AAM prepared in $C_2H_2O_4$ is much higher than that of AAM prepared in H_2SO_4. The PL intensity and peak position depend strongly on the excitation wavelength. All the emission and excitation spectra are composed of two contributions, and there is a good fit taking into account two Gaussian fit peaks. For emission spectra, one of the peaks is situated at a constant wavelength of 460 nm, and the other shifts to longer wavelength along with the excitation wavelength, while for excitation spectra, one of the peaks is situated at a constant wavelength of 285 and 265 nm for AAM prepared in $C_2H_2O_4$ and in H_2SO_4, respectively, and the other also shifts to longer wavelength along with the emission wavelength. Annealing treatment of the as-prepared AAM results in an apparent reduction of the intensity of the emission at shorter excitation wavelength, while at longer excitation wavelength (longer than 320 nm) the emission intensity firstly increases, and at $500\,°C$ reaches a maximum value, then decreases. Even after annealing treatment at $900\,°C$ the PL intensity is still very strong. The first PL peak intensity increases with excitation wavelength at the same annealing temperatures. It is considered that there are two PL centres, one originating from the oxygen-related defects in the barrier layer, contributing mainly to the second PL band, and the other correlated with the aluminum incorporated into the anion-contaminated alumina layer in the AAM, contributing mainly to the first PL band.

Our study demonstrates that when using AAM as a template to synthesize new luminescence materials, care must be taken to investigate the PL mechanisms of the template

because its PL properties depend not only on the excitation wavelength but on the annealing temperature as well.

Acknowledgment

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