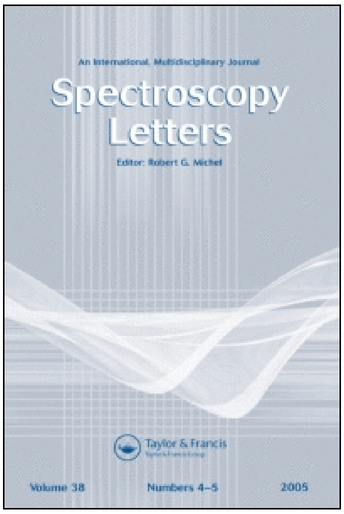

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ENHANCED PHOTOLUMINESCENCE OF Eu(III)-ANCHORED POROUS ANODIC ALUMINA FILM

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ENHANCED PHOTOLUMINESCENCE OF Eu(III)-ANCHORED POROUS ANODIC ALUMINA FILM

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ABSTRACT

We report here the enhanced luminescence of Eu(III)-anchored porous anodic alumina prepared by self-assembling Eu(III) acetylacetonate, and investigate the luminescence mechanisms. Porous anodic alumina can emit visible light due to a lot of oxygen vacancies formed in the anodic oxidation. The existence of oxygen vacancies resulted in e^--h^+ pairs when excited. Eu(II) exists stably by forming Eu^{2+}-hole complexes. The enhanced luminescence of Eu(III)-anchored porous anodic alumina is attributed to the complex luminescence of e^--h^+ through luminescence center Eu^{2+}.

Key Words: Porous anodic alumina; Enhanced fluorescence; Complex luminescence

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INTRODUCTION

Photo-properties of rare earth ions doped in alumina film which was prepared by sol-gel method, have been reported[1], but that based on porous anodic alumina (AAO) are rarely detailed. An anodic oxide film formed on aluminum can emit visible light, i.e., photoluminescence (PL) when illuminated with UV radiation[2]. Zhang et al. found that photoluminescence of porous alumina film prepared in $C_2H_2O_4$ and H_2SO_4 increased with increasing heat-treatment temperature[3]. Meanwhile, the optical properties of rare earth ions have become recent areas of research because of their potential for utilization in optical memory chips[4], and solid-state lasers[5]. However, no reports about photoluminescence of Eu^{3+}- AAO have been published.

In this letter, the enhanced fluorescence of Eu(III)-anchored porous anodic alumina film was observed and the luminescence mechanisms were discussed. Eu(III) acetylacetonate was grafted on porous anodic alumina by self-assembling. We investigated its formation and confirmed its presence by XPS.

EXPERIMENTAL

The anodizing of the Al plate (99.999% aluminum, dimensions of 30×10 mm) was carried out at a constant voltage of 80 V in a 0.5 mol/L phosphoric acid bath at room temperature for 30 min, to obtain AAO film with the average pore size of 100 nm. The morphology of the porous anodic alumina membrane was observed using Transmission Electron Microscopic (TEM) image recorded with a Hitachi-600 microscope (Fig. 1). The porous anodic alumina, with aluminum, was immersed in an aqueous solution of 0.1 mol/L europium acetylacetonate for 6 h and 24 h at room temperature, separately. Then they were sonicated and washed with deioned water and absolute ethanol several times to remove physical adsorption of europium acetylacetonate.

X-ray Photoelectron Spectroscopy (XPS) (V.G. ESCA Lab 220I-XL photoelectron spectrometer, Al K_α source) was used to confirm the presence of Eu(III) in the Eu(III)-anchored alumina. The fluorescence spectra were measured using a Hitachi M-850 fluorescence spectrophotometer. The light source for excitation was from a 150 W Xe lamp. The emitted light was detected with an R3788 photomultiplier tube with a set resolution of 1.0 nm.

RESULTS AND DISCUSSION

The anchoring of europium(III) acetylacetonate on the porous alumina support was accomplished via the replacement of the ligand (L) by a

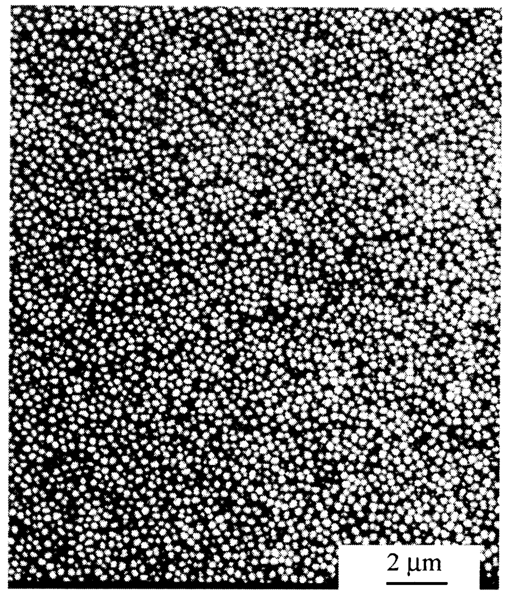


Figure 1. TEM image of porous anodic alumina film.

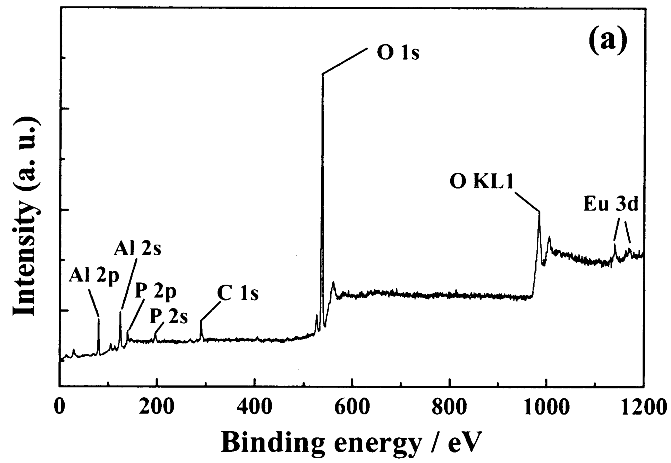
surface proton, which reciprocates by forming a stable molecule with the anion. This process facilitates ligand removal and is accompanied by the introduction of surface −O−M (M = Al,Si, . . .) in the metal complex according to[6]

$$Me^{n+}L_n + m(M\text{–}OH) \rightarrow Me^{n+}(L_{n-m})(\text{–}O\text{–}M)_m + mHL$$

It is found that the europium(III) ions are preferentially coordinated with Al-O polyhedral and the covalence of the Eu−O bond is decreased by the coordinated Al^{3+} ions[7].

Figure 2a shows the XPS survey spectrum for the Eu^{3+}-anchored alumina which exhibits the characteristic O1s (531 eV), Al 2s (119 eV) and Al 2p (74 eV) peaks associated to the AAO film. The peaks of P 2s (191 eV) and P 2p (133 eV) originate from the PO_4^{3-} ions incorporated into the AAO film during the anodic oxidation. The peaks of C1s (285 eV), Eu 3d5 (1136 eV) and Eu 3d3 (1166 eV) are due to the anchoring of Europium(III). The Eu 3d5 (1136 eV) and Eu 3d3(1166 eV) level spectrum is shown in Figure 2b.

In Figure 3, the photoluminescence (PL) spectrum of the AAO film displays a narrow blue-green emission centered at 397 nm. PL in this



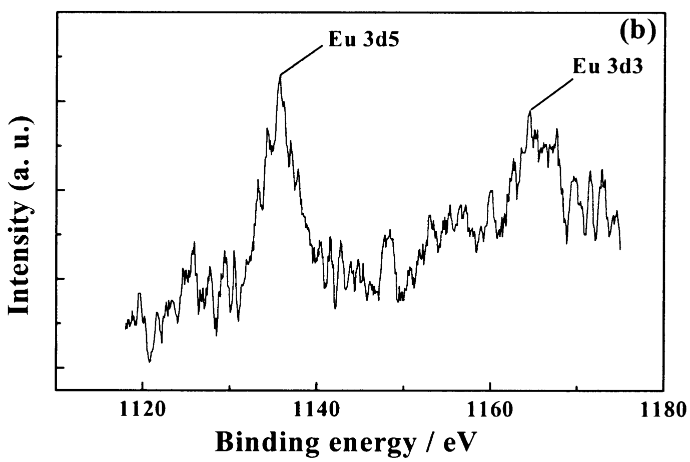


Figure 2. The XPS spectra of the Eu(III)-anchored porous alumina (AAO) film a) the XPS survey spectrum; b) the Eu 3d level spectrum.

spectral region is attributed to the presence of oxygen vacancies associated with electrons localized on the bridge oxygen atoms in the lattice. This emission results from the recombination of photogenerated charge carriers in shallow traps. From the PL spectra, it can also be seen that the AAO film derived from H_3PO_4 shows a stronger fluorescence than the film prepared in H_2SO_4 and exhibits a blue shift band. This enhancement may

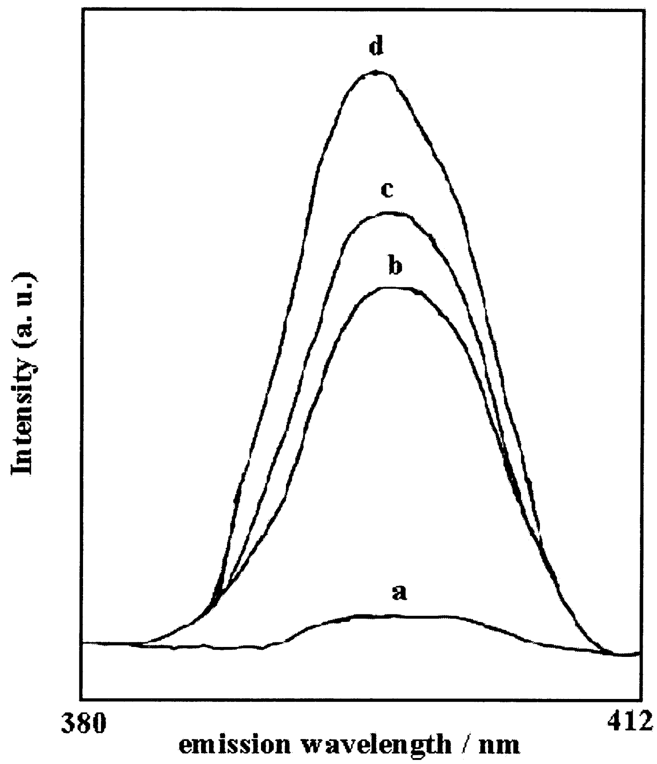


Figure 3. The photoluminescence spectra of the porous alumina film derived from 0.5 mol/L H_2SO_4 (a); derived from 0.5 mol/L H_3PO_4 (b); the Eu(III)-anchored porous alumina for 6 h (c); 24 h (d) ($\lambda_{ex} = 310$ nm).

be attributed to the incorporation of PO_4^{3-} except for the existence of many singly ionized oxygen vacancies (F^+ centers) during the anodic proceeding[3].

Figure 2 also presents Eu(III)-anchored porous anodic alumina film in the wavelength range of 380 ~ 412 nm. Clearly, the intensity of the PL band of Eu(III)-anchored porous alumina further increases in comparison with the unanchored alumina. Moreover, it was noticed that the longer anchoring time, the more enhanced PL intensity due to the more Eu(III) anchored. No emission that corresponds to $^5D_0$-^7F_j where j = 0,1,2,3,4 and displays in wavelengths from 580 to 700 nm was found even if excited at 394 nm, which comfirms the absence of Eu^{3+}. Then Eu must exist at its +2 valence during luminescing[8].

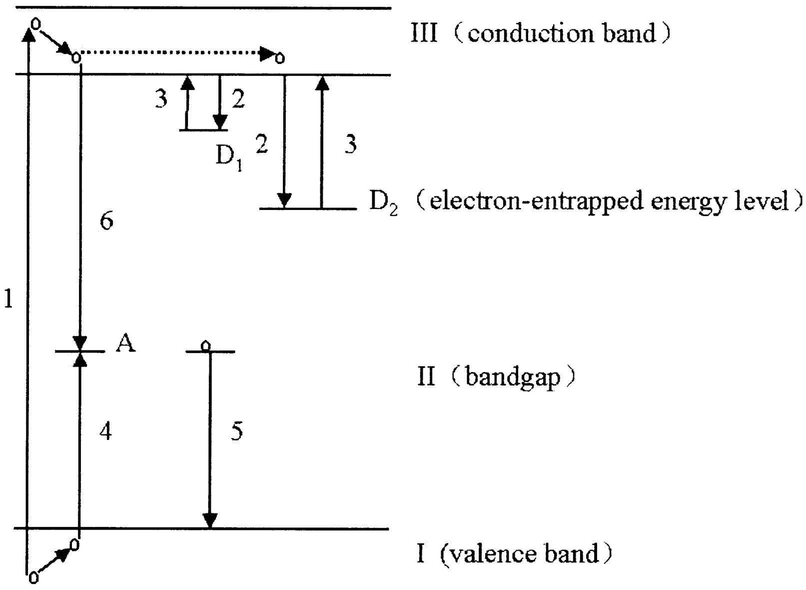


Figure 4. The Schon-Klasens model.

Due to the singly ionized oxygen vacancies in AAO[3], there would be e^{-}-h^{+} pairs when the sample was excited by UV light[9]. The defects or ejected electrons that stem from these carriers are free to move about and can be effectively harvested for the reduction of high oxidation states rare-earth metal ions to their corresponding low oxidation state ions. When Eu^{3+} is grafted on AAO, the ejected electrons from the oxygen-associated hole centers react with Eu^{3+} to produce Eu^{2+} ions, which have been proposed to become stable by forming Eu^{2+}-hole complex[10]. The outer electrons of Eu^{2+} were strongly affected by their surrounding field, so that they can enter the conduction band and take part in photoconduction. The luminescence spectra were not determined by energy structure of Eu^{2+}, but by property of the whole complex, which was called complex luminescence. Photoluminescence was caused by electron-hole through luminescence center. The phenomenon can be well illustrated by Schon-Klasens model (Fig. 3)[8].

Electrons and holes in porous anodic alumina can freely move about in the energy band to produce photoconduction (process 1). A small amount of Eu^{2+} engendered an impurity center in the forbidden band, i.e., luminescence A. Because of thermodynamic equilibrium, electrons soon were reduced to the bottom of conduction band, reversibly, holes to the top. Electrons can be effectively harvested by the electron trap D (process 2) when diffusing in conduction band, and they would not be released until they accepted energy (from infrared light or by heat-treatment) (process 3). On the other hand, holes can be trapped by unionized luminescence center A (process 4), and they may return to conduction band due to thermo-disturbance (process 5). Luminescence was caused by multiplex of conduction band electrons and holes on luminescence center A (process 6). Therefore, AAO played a major role. As we can see, the shape and emission wavelength of Eu^{3+}-AAO luminescence band was similar to that of AAO. A stronger intensity was caused by Eu^{2+}. However, the luminescence mechanisms were not different at all.

In conclusion, the enhanced luminescence of Eu^{3+}-anchored porous anodic alumina is attributed to the multiplex luminescence.

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