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ScienceDirect
Journal of Luminescence 122–123 (2007) 876–878
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Influence of annealing temperature on photoluminescence characteristics of Gd_2O_3:Eu/AAO nanowires

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Available online 15 March 2006

Abstract

One dimensional Gd_2O_3:Eu nanowires with diameters of ~100 nm were fabricated by anodic aluminum oxide (AAO) template method. Excitation and emission spectra, fluorescence dynamics of Gd_2O_3:Eu/AAO were studied. The results showed that the charge transfer band of Eu^{3+} in Gd_2O_3:Eu/AAO blue shifted with increasing annealing temperature and time. The decay time constant of $^5D_0$–$^7F_2$ transition became longer with the increasing annealing temperature in Gd_2O_3:Eu/AAO. The $^5D_0$–$^7F_1$ transition of Eu^{3+} ions in cubic phase had longer lifetime than that in amorphous phase. In contrast to the lifetime of $^5D_0$–^7F_J in the bulk powder, that in Gd_2O_3:Eu/AAO composite films increased.

Keywords: Gd_2O_3:Eu nanowires; Template method; Photoluminescence characteristics

1. Introduction

The anodic aluminum oxide (AAO) template is effective for preparation of ordered nanostructure with controlled morphologies and properties, because of its uniform and nearly parallel porous structure. This offers a promising route to prepare ordered nanostructure materials with controlled morphologies and properties. The AAO template has been widely used to prepare metal [1–3] or semiconductor nanowires [4]. However, rare-earth (RE) oxide nanostructures prepared using the AAO template is quite rare [5,6]. And more, the luminescent properties of RE oxide in the AAO template have not been studied carefully. Recently, we successfully fabricated assemble Gd_2O_3:Eu nanowires using the template method. In this paper, we demonstrate the dependence of structural and luminescent properties on annealing temperature.

2. Experimental

Appropriate amounts of Gd_2O_3 (4N) and Eu_2O_3 (4N) (95:5 mol ratio) were dissolved in concentrated HNO_3 firstly by stirring the mixture at about 90 °C, and then naturally cooling down. After this solution was added appropriate amounts of deionized water to form a 0.05 M aqueous solution of nitrate and appropriate amounts of urea was added into the solution. The AAO template was dipped into above mentioned Gd_2O_3:Eu precursor solution at 80 °C, removed and dried in air for 10 h. Subsequently, composite films were placed in a furnace and heated at 500, 600 and 800 °C for 3 h. Corresponding samples were labeled A, B and C, respectively. The samples heated at 1000 °C for 3 and 5.5 h were labeled D, E, respectively. The surface films were removed by polishing the template, washed with deionized water and dried in air. Finally, the Gd_2O_3:Eu/AAO were obtained.

The morphologies of the AAO template and the Gd_2O_3:Eu/AAO were characterized by a JEOL JXA-840 SEM and JEOL JEM-2010 TEM. The X-ray diffraction (XRD) was examined by a Rigaku Dmax-B X-ray

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doi:10.1016/j.jlumin.2006.01.314

diffractometer. Excitation spectra were recorded using a Hitachi F-4500 spectrophotometer. In the measurements of high-resolution emission spectra and fluorescence dynamics, the samples were pumped by a 266-nm laser generated from the pulsed Nd:YAG (aluminumgarnet) combine with a Fourth-Harmonic-Generator. A Spex 1403 spectrometer, a photon multiplier and a boxcar integrator were used for recording the fluorescence spectra. Fluorescence dynamics were recorded by a TEKTRONIX TDS-3052 oscilloscope.

3. Morphology and structure

Figs. 1(a)–(c) show the SEM and TEM images of the AAO template, Gd_2O_3:Eu/AAO nanowires and Gd_2O_3:Eu nanowire, respectively. From Fig 1(a) it can be seen that pores of the template are uniformly distributed and the pore diameter is about 100 nm. Fig. 1(b) shows that ordered nanowires are formed in the channels of template, which parallels to each other. In Fig. 1(c), a single nanowire in the sample D is observed by the TEM image. The selective area electron diffraction pattern (SAED, see the inset of Fig. 1(c)) taken from the single nanowire shows that the Gd_2O_3:Eu nanowire is a single crystal.

The XRD patterns of various G_2dO_3:Eu/AAO samples were measured. The results showed that the AAO template and Gd_2O_3:Eu nanowires were both amorphous materials when the annealing temperature was lower than 800 °C (samples A, B, C). As the annealing temperature increased to 1000 °C, the AAO template was partly crystallized and cubic Gd_2O_3 was formed (samples D and E).

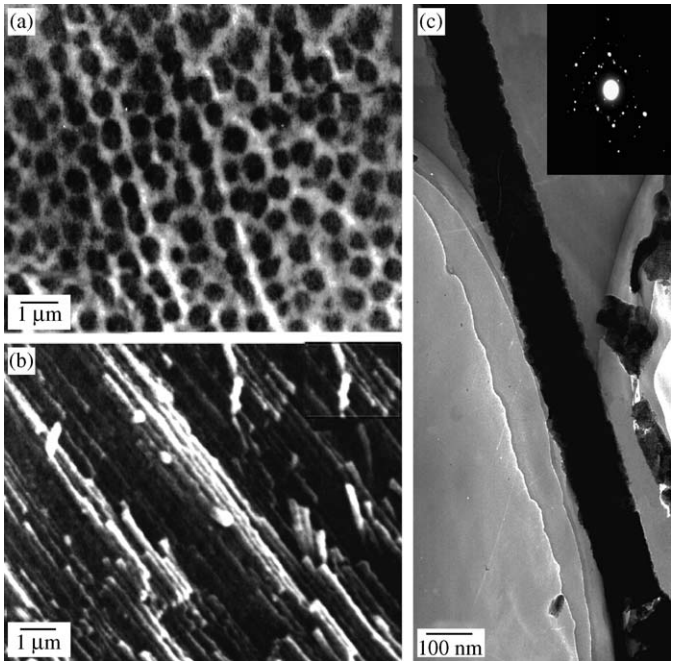

Fig. 1. (a) SEM image of AAO template, (b) SEM image of Gd_2O_3:Eu/AAO annealing at 1000 °C, (c) TEM images of Gd_2O_3:Eu nanowire annealing at 1000 °C; Inset: SAED pattern.

4. Spectroscopic results

Excitation spectra of various Gd_2O_3:Eu/AAO and the Gd_2O_3:Eu bulk powder (labeled with H) at room temperature are shown in Fig. 2. In the bulk, three excitation peaks are observed, at 231, 254 and 277 nm, respectively. They are corresponding to the excitonic absorption, the CT transition and the absorption of Gd^{3+} from $^8S_{7/2}$ to $^6I_{7/2}$, respectively [7]. In the Gd_2O_3:Eu/AAO, the excitonic absorption band disappears completely, which may be attributed to the quenching of exciton transition due to a number of involved surface defect states. The location of the CT transition is nearly same with that in the bulk as the annealing temperature is 500 °C and shifts blue with increasing the annealing temperature. The absorption location of Gd^{3+} does not change in different samples.

Fig. 3 shows high-resolution emission spectra of Eu^{3+} in different samples. The $^5D_0$–^7F_J ($J = 0, 1, 2, 3, 4$) can be observed in all the Gd_2O_3:Eu/AAO. In comparison to the bulk (cubic), the $^5D_0$–^7F_J transitions in Gd_2O_3:Eu/AAO are broadened greatly due to disordered local environments surrounding the Eu^{3+} ions. In the samples D and E, three narrower $^5D_0$–$^7F_1$ lines can be distinguished. They are overlapped on the broader lines of $^5D_0$–$^7F_1$. The locations of the three lines are at 586, 592 and 597.5 nm, respectively, which are same as those in the bulk. These sharper lines originate from emissions of Eu^{3+} at C_2 symmetry sites. The intensity ratios of $^5D_0$–$^7F_2$ /$^5D_0$–$^7F_1$ of Eu^{3+} in various samples are calculated, as listed in Table 1. It is apparent that the intensity ratio of $^5D_0$–$^7F_2$ / $^5D_0$–$^7F_1$ decreases with the increasing annealing temperature as well as annealing time, implying that the covalence of Eu–O bonds decreases and the symmetry increases.

The fluorescent decay curves for the $^5D_0$–$^7F_2$ transitions of Eu^{3+} ions at 612 nm in different samples were measured and fitted. The exponential decay time constant in different

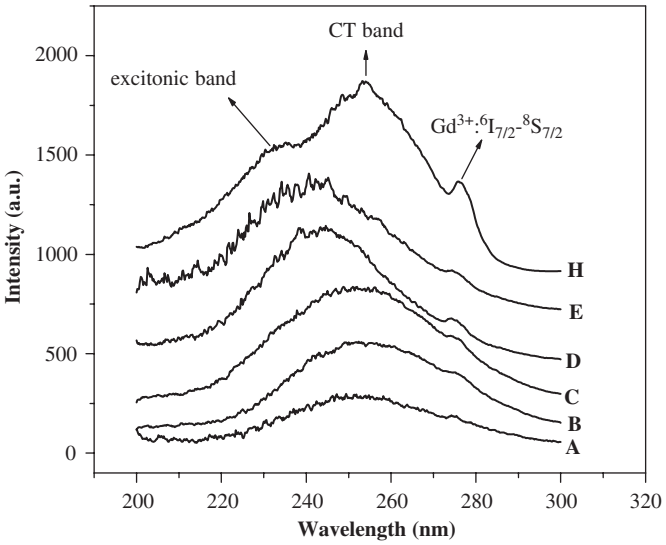

Fig. 2. Excitation spectra of Eu^{3+} in different Gd_2O_3:Eu/AAO and in the bulk Gd_2O_3: Eu ($\lambda_{em} = 611\,nm$).

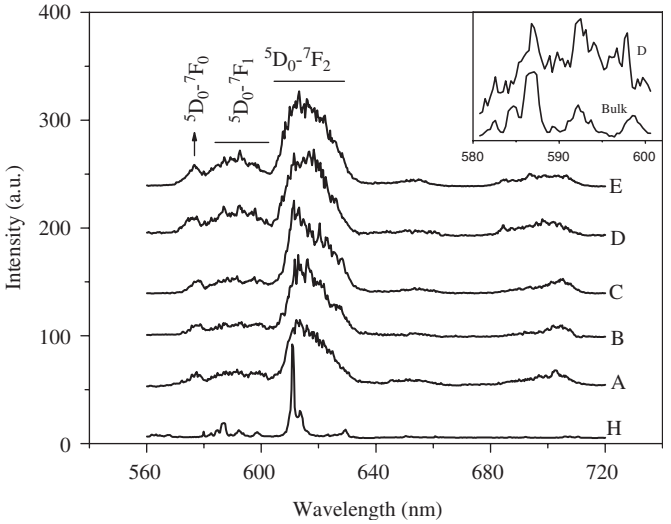

Fig. 3. High-resolution emission spectra of $^5D_0$–^7F_J $(J = 0, 1, 2, 3, 4)$ transitions in different Gd_2O_3:Eu/AAO and bulk Gd_2O_3:Eu ($\lambda_{ex} = 266\,nm$); Inset: magnification of the $^5D_0$–$^7F_1$ transitions.

Table 1
Variation of CT band, intensity ratio of $^5D_0$–$^7F_2$/$^5D_0$-$^7F_1$ and decay time constant of the $^5D_0$–$^7F_2$ transition (at 611 nm) of Eu^{3+} ions

Samples	CT band (nm)	I_2/I_1	Decay time constant (ms)
A	253	6.13	1.25
B	252	5.22	1.26
C	251	5.08	1.43
D	244	3.08	1.68
E	239	3.08	2.07
H	254	2.55	1.13

samples were obtained by fit, as listed in Table 1. It is apparent that the decay time constant of $^5D_0$–$^7F_2$ transition becomes longer with the increasing annealing temperature in Gd_2O_3: Eu/AAO. This indicates that the local environments surrounding Eu^{3+} ions become relative order when the annealing temperature is high. In that case, the nonradiative relaxation between Eu^{3+} ions and defect states will decrease, leading to the increase of fluorescence decay time. In comparison to the bulk, the fluorescence lifetime of Eu^{3+} ions of Gd_2O_3:Eu/AAO become longer. This is attributed to the influence of refractive index of the surrounding medium [8] on the radiative lifetime.

The fluorescent decay curves for the $^5D_0$–$^7F_1$ transitions of Eu^{3+} were also measured. The results indicate that for the $^5D_0$–$^7F_1$ transitions, there exist two decay time constants, a faster (τ_1) and a slower (τ_2), as listed in Table 2. The values of decay time constants τ_1 and τ_2 in different locations are nearly same. This is assigned to the

Table 2
Fluorescence lifetimes for the $^5D_0$–$^7F_1$ transition of Eu^{3+} ions in the Gd_2O_3: Eu/AAO annealed at 1000 °C for 3 h (sample D)

Monitoring λ (nm)		586	592	597.5
Lifetime (ms)	τ_1	1.12	1.11	1.01
	τ_2	3.43	3.48	3.03
Ratio constant	I_1	0.40	0.36	0.45
	I_2	0.60	0.64	0.55

$^5D_0$–$^7F_1$ emissions of Eu^{3+} ions locating at two different phases, the Eu^{3+} ions in amorphous phase and those in cubic phase, which has been certified by high-resolution spectra and XRD patterns. The $^5D_0$–$^7F_1$ emission for Eu^{3+} in the cubic phase has slower decay time constant than that in the amorphous phase owing to decreased nonradiative relaxation.

5. Conclusions

The uniform nanowires of Gd_2O_3:Eu were fabricated in AAO template. As the annealing temperature approaches 1000 °C, cubic Gd_2O_3:Eu is formed partly. The charge transfer band of Eu^{3+} ions in Gd_2O_3:Eu/AAO shifts blue with increasing annealing temperature and time, and the decay time constant of $^5D_0$–$^7F_2$ transition increases in Gd_2O_3:Eu/AAO. Two spectral components of the $^5D_0$–$^7F_1$ transitions are identified by fluorescent dynamics, corresponding to Eu^{3+} ions in amorphous phase and cubic phase. The radiative lifetime of Eu^{3+} in Gd_2O_3:Eu/AAO become longer in comparison to that in the bulk due to influence of the surrounding media.

Acknowledgments

This work is supported by the National Nature Science Foundation of China (Grants 10374086) and Talent Youth Foundation of JiLin Province (Grants 20040105).

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