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Photoluminescence behaviors of Eu-doped $GdVO_4$ thin film phosphors grown by pulsed laser ablation

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Abstract

$GdVO_4:Eu^{3+}$ thin films have been grown on Si (1 0 0) substrates using pulsed laser deposition. The films deposited at the different conditions show different microstructural and luminescent characteristics. The crystallinity, surface morphology and photoluminescence of the films are highly dependent on the deposition conditions, oxygen pressure and substrate temperature. The photoluminescence results obtained from $GdVO_4:Eu^{3+}$ films grown under optimized conditions have indicated that Si (1 0 0) is promising substrate for the growth of high quality $GdVO_4:Eu^{3+}$ film phosphor. In particular, the surface morphology and photoluminescence of $GdVO_4:Eu^{3+}$ films show very similar behavior as a function of oxygen pressure. The emitted radiation was dominated by the red emission peak at 620 nm and this phosphor is promising for applications in flat panel displays.

Keywords: $GdVO_4:Eu^{3+}$; Phosphors; Thin films; Laser processing; Luminescence

1. Introduction

Phosphors are applied to faceplates either in powder or thin-film form. In 1980, Robertson and van Tol [1] found that rare-earth-ion-doped garnet luminescent films epitaxially grown on single-crystal substrates could withstand much higher power densities than with powder phosphors without tube degradation. Since then thin-film phosphors have been attracting much attention in high-resolution devices such as cathode-ray tubes (CRTs) and flat-panel display devices [2–6]. Thin-film phosphors have been prepared by a variety of deposition techniques, such as sol–gel process [7], chemical vapor deposition [8], spray pyrolysis [9], and pulsed laser deposition [10]. Recently, the pulsed-laser deposition (PLD) has been used for the growth of oxide thin-film phosphors [11,12]. In thin film phosphors, brightness may be associated with several factors such as interactions between the substrate and generated light in film, the film processing conditions, and the composition of the film.

An improved performance of displays and lamps requires high quality of phosphors for sufficient brightness and long-term stability. Recently, $GdVO_4$ has attracted great interest as an excellent laser medium and as a host material for rare earth ions in luminescent displays [13–16]. Because of a strong absorption to ultraviolet light by $GdVO_4$, an effective energy transfer from ${VO_4}^{-3}$ to Eu^{3+} and effective excitation of Eu^{3+} by the 450 nm strong emission of ${VO_4}^{-3}$, $GdVO_4:Eu^{3+}$ is a highly efficient red light-emitting material.

$GdVO_4$ has $ZrSiO_4$ structure, belonging to the space group *IA/amd* (Gd^{3+}, V^{5+} and O^{2-} occupy the positions 4a (0 0 0), 4b(0 0 0.5) and 16 h (0 x z), respectively) [17]. It is tetragonal system and its lattice parameters are $a = 7.2176$ Å, $c = 6.3483$ Å, $Z = 4$, $D_x = 5.474\ g/cm^3$ [18]. For the given

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substrate, by changing the deposition conditions, especially oxygen pressure and substrate temperature, the different crystallinity and surface morphology of the films have been induced. Then, under the optimized conditions we could improve the crystallinity, surface morphology and luminescent characteristics. In this paper, we report the luminescent behaviors of $GdVO_4:Eu^{3+}$ thin films.

2. Experiments

$GdVO_4:Eu^{3+}$ powder samples were prepared from stoichiometric amounts of Gd_2O_3 (99.9%, Aldrich), V_2O_5 (>99.6%, Aldrich) and Eu_2O_3(99.99%, Aldrich, the molar ratio of $Eu^{3+} = 0.03$). For ceramic target, the powder mixture was pelletized into a disk and sintered at 950 °C for 2 h. The films were grown by laser ablation method using an ArF excimer pulse laser with a wavelength of 193 nm. The distance between target and substrate was kept at 32–35 mm. The laser flux was approximately 3.5 J/cm^2 and repetition rate was 5 Hz. The thin films were deposited on Si (1 0 0) substrates at the oxygen pressures of 100, 150, 200, 250, 300, 350 or 400 mTorr and substrate temperature, 600 °C. And the films are also grown at the fixed oxygen pressure of 300 mTorr under the substrate temperatures 500, 600 or 700 °C. The structural characteristics of the films were analyzed by using X-ray diffraction (XRD, Philips, X'pert). The thicknesses of the films, measured by scanning electron microscope, were approximately 600 nm and surface morphology and roughness of the films were measured by atomic force microscope (AFM). The photoluminescence (PL) spectra were measured at room temperature using a luminescence spectrometer (Perkin-Elmer, LS50B) and excitation by a broadband incoherent ultraviolet light source with a dominant excitation wavelength of 254 nm.

3. Results and discussions

Fig. 1 shows the changes in the XRD patterns of $GdVO_4:Eu^{3+}$ films grown at substrate temperature 600 °C with the different oxygen pressures of 100, 150, 200, 250, 300, 350 or 400 mTorr. For oxygen pressures less than 150 mTorr, the film orientation was preferentially (2 0 0) and as the oxygen pressure was increased above 150 mTorr, the film crystallinity has been changed to the polycrystalline structure with (1 0 1), (2 0 0), (1 1 2), (3 0 1) and (1 0 3) peaks. The change in film orientation is believed to be associated with an increase in the number of density of species on the film surface with increase in oxygen pressure [19]. An increased number density of species on the film surface can result from the enhanced chance of formation of clusters of ablated species in the laser plume at higher oxygen pressure [20]. As the oxygen pressure increases above 150 mTorr the crystallinity of the films improved. Especially, the FWHM of the (1 0 1) peaks are narrower (∼15%) for the film grown at 300 mTorr than for the film grown at 200 mTorr, indicating the better crystallinity of the former than of the later.

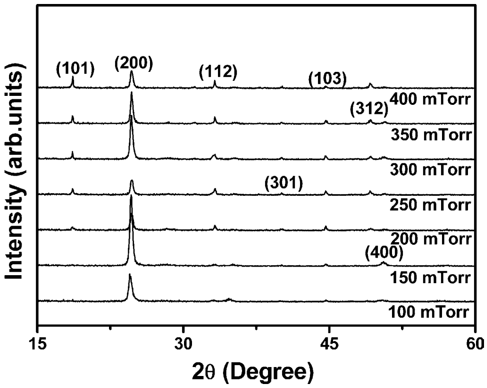

Fig. 1. XRD patterns of $GdVO_4:Eu^{3+}$ films deposited on Si (1 0 0) substrate at the substrate temperature 600 °C with the different oxygen pressures of 100, 150, 200, 250, 300, 350 or 400 mTorr.

Surface morphology and roughness of the phosphor thin films has strong effects on the PL response of the films. Table 1 shows the grain size and root mean square (rms) surface roughness of $GdVO_4:Eu^{3+}$ films as a function of the amount of oxygen pressure. The average grain size of $GdVO_4:Eu^{3+}$ films increases from ∼92 nm ($P(O_2) = 100$ mTorr) to ∼293 nm ($P(O_2) = 300$ mTorr) with increasing oxygen pressure, while the initial increase in grain size of $GdVO_4:Eu^{3+}$ films decreases as the oxygen pressure increases from $P(O_2) = 300$ mTorr to $P(O_2) = 400$ mTorr (∼247 nm). The AFM data also show that films with different surface roughnesses were obtained by changing the oxygen pressure. The rms roughnesses of these films show the similar behavior to the grain size as the oxygen pressure changes. The rms roughness of these films was found to increase from ∼1.4 nm ($P(O_2) = 100$ mTorr) to ∼9.8 nm ($P(O_2) = 300$ mTorr) with increasing oxygen pressure, while the initial increase in rms roughness value decreases as oxygen pressure increases from 300 to 400 mTorr (∼8.7 nm). The increase in rms values with increase of oxygen pressure (to $P(O_2) = 300$ mTorr) is attributed to the larger grain size. Due to the increase in grain size, the density of grain boundaries in $GdVO_4:Eu^{3+}$ film grown at 300 mTorr is smaller than the films grown at the other oxygen pressures. Furthermore, these grain boundaries may absorb and/or scatter light generated

Table 1
Average grain size and rms surface roughness of $GdVO_4:Eu^{3+}$ films as a function of oxygen pressure

Oxygen pressure (mTorr)	Average grain size (nm)	RMS surface roughness (nm)
100	92	1.4
150	123	6.1
200	154	7.1
250	185	8.5
300	293	9.8
350	266	9.0
400	247	8.7

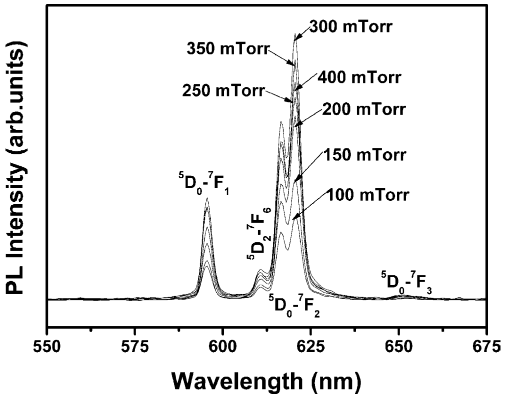

Fig. 2. A comparison of the room temperature PL spectra of $GdVO_4$:Eu^{3+} films as a function of oxygen pressure.

inside the film resulting in lower PL brightness, since the $GdVO_4$:Eu^{3+} film grown at 300 mTorr with less grain boundaries exhibited superior PL properties as reported below.

Fig. 2 shows the room temperature PL spectra from $GdVO_4$:Eu^{3+} films as a function of the oxygen pressure. The emitted radiation was dominated by the red emission peak at 620 nm. Due to the shielding effect of 4f electrons by 5s and 5p electrons in outer shells in the europium ion, narrow emission peaks are expected, consistent with the sharp peak in Fig. 2. The characteristic emissions of Eu^{3+} were observed, including those peaking ant 610, 616 and 620 nm for $^5D_0$-$^7F_2$ transition, at 595 nm for $^5D_0$-$^7F_1$ transition and at 652 nm for $^5D_0$-$^7F_3$ transition. As shown in Fig. 3, $GdVO_4$:Eu^{3+} films have maximum PL intensity at the oxygen pressure of 300 mTorr and the brightness of the films was increased by a factor of 2.5 in comparison with that from $GdVO_4$:Eu^{3+} film grown at 100 mTorr. The improvement in PL performance with increasing oxygen pressure may result not only from improved crystallinity leading to higher oscillating strengths for the optical transitions [21], but also from reduced internal reflections of the emitted light due to rougher surfaces [22]. The increased crystallite size in $GdVO_4$:Eu^{3+} films by increasing oxygen pressure could also result from less grain boundary absorption as discussed above.

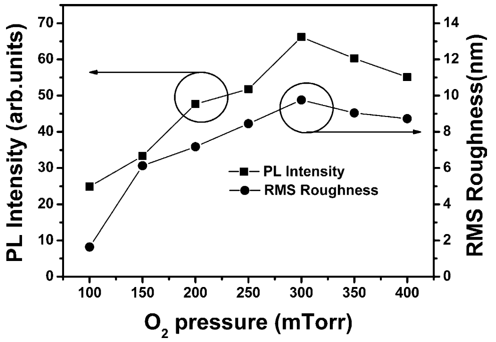

Fig. 3. Plots of PL brightness and the rms roughness of $GdVO_4$:Eu^{3+} films as a function of oxygen pressure.

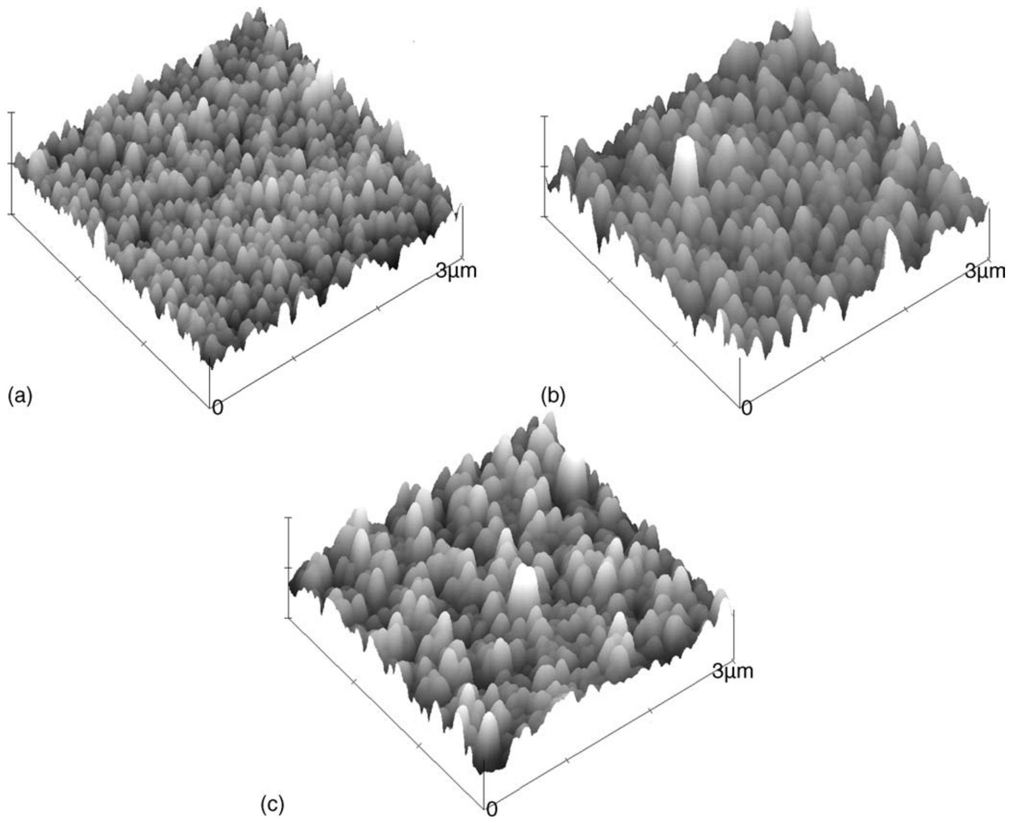

Fig. 4. AFM images of the $GdVO_4$:Eu^{3+} films with different substrate temperature (a) 500; (b) 600; and (c) 700 °C.

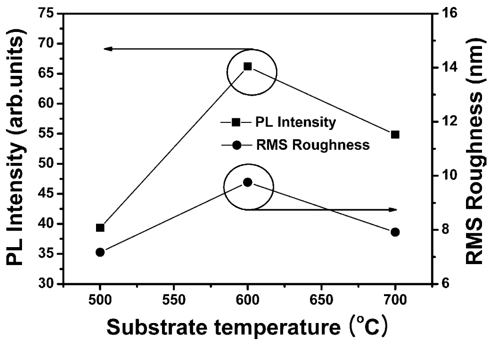

Fig. 5. Plots of PL brightness and the rms roughness of GdVO$_4$:Eu^{3+} films as a function of substrate temperature.

The correlation between PL brightness and the rms roughness of GdVO$_4$:Eu^{3+} films are shown in Fig. 3 as a function of oxygen pressure. The PL intensity and rms roughness have similar behavior as a function of oxygen pressure. Films with different roughnesses were obtained by changing the oxygen pressure during the film growth. As shown in Fig. 3, the film grown at the oxygen pressure of 300 mTorr has rougher surface than films grown at any other oxygen pressures. The root mean square (rms) roughness of these films was found to increase from ∼1.6 to ∼9.7 nm with increasing oxygen pressure from 100 to 300 mTorr, while the initial increase in rms roughness decreases from 9.7 to 8.7 nm as oxygen pressure increases from 300 to 400 mTorr. It is clear from this figure that PL brightness and rms roughness are highest at $P(O_2) = 300$ mTorr. Note that the PL intensity and rms roughness for GdVO$_4$:Eu^{3+} films increase uniformly with increasing oxygen pressure to 300 mTorr, while the initial increase in intensity of the film decreases as the oxygen pressure increases from $P(O_2) = 300$ mTorr to $P(O_2) = 400$ mTorr.

Fig. 4a–c shows the AFM images of GdVO$_4$:Eu^{3+} films grown at oxygen pressure 300 mTorr with different temperatures 500, 600 and 700 °C, respectively. The AFM measurements of the films grown at different temperatures have shown that rms roughness of these films was found to increase from ∼7.1 to ∼9.7 nm with increasing substrate temperature from 500 to 600 °C, while the initial increase in rms roughness decreases from 9.7 nm to 7.9 nm as substrate temperature increases from 600 to 700 °C. Shown in Fig. 5 are the plots of PL brightness and rms roughness of GdVO$_4$:Eu^{3+} films as a function of substrate temperature. According to the results of the Fig. 5, the initial improvement in PL performance is probably brought about by reduced internal reflections caused by rougher surfaces of the films. It can be suggested that the PL intensity strongly depends on the morphology and rms roughness of the films.

4. Conclusions

In summary, high-quality GdVO$_4$:Eu^{3+} thin-film phosphors have been deposited on a Si (1 0 0) substrates using laser ablation method. The crystallinity, surface roughness and photoluminescence of thin film phosphors are highly dependent on the deposition conditions, in particular, the oxygen pressure and substrate temperature. By changing oxygen pressure and substrate temperature, we could improve the luminescent characteristics under the optimized conditions. Improved PL brightness with increasing oxygen pressure is suggested to result not only from improved crystallinity leading to higher oscillating strengths for the optical transitions, but also from reduced internal reflections caused by rougher surfaces. The rms surface roughness and PL intensity of the films also behave similarly as a function of oxygen pressure. And, an increase in oxygen pressure from 100 to 300 mTorr resulted in an increase in both rms surface roughness and PL intensity. Growth of as-deposited GdVO$_4$:Eu^{3+} thin-film with high brightness is very encouraging for the applications of thin-film phosphors in display technologies.

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