

Luminescence Characteristics of Red Light Emitting YVO₄:Eu Thin-Film Phosphors Deposited on Si Substrate Using Pulsed Laser Deposition

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Europium doped yttrium vanadate (YVO₄:Eu) phosphor thin films were grown using a pulsed laser deposition (PLD) technique on silicon substrate. The structural characterization carried out on a series of YVO₄:Eu films at post annealing temperature in the range of 550 °C-1150 °C indicating that films were preferentially (200) oriented at post annealing temperature above 950 °C. Photoluminescence of thin film increased with the increase of post annealing temperature and ambient oxygen pressure though the thin film has the powder-like surface morphology at oxygen pressure above 200 mTorr. Photoluminescence decay from ⁵D₁ level of Eu³⁺ show the great concentration dependency, which can be used as a good parameter to control the composition of YVO₄:Eu thin film.

Key Words : Yttrium vanadate, Phosphor, Thin film, Pulsed laser deposition

Introduction

The development of new types of flat panel and projection displays has created a need for optical phosphors with new or enhanced properties. The interest in phosphor nanocrystalline thin films has been growing because of their potential application in high resolution devices such as flat panel devices. Displays with thin film phosphors have higher contrast, resolution and thermal conductivity as well as a high degree of uniformity and better adhesion.¹ Most of phosphor materials consist of multi-components from 3 to 5, and their luminescence efficiency is largely affected by concentration of activator which is responsible for luminescence of phosphor.² One of the most important things in deposition of phosphor thin film is stoichiometric transfer of target material to substrate. It is well known that the pulsed laser deposition(PLD) can produce a wide variety of complex compounds with controlled compositions and properties.³

YVO₄ has been widely used as a host lattice for lanthanide ions to produce phosphors emitting a variety of colors.⁴ Eu³⁺-activated YVO₄ is an important commercial red phosphor used in the cathode ray tube displays, the high pressure mercury lamp, thermographic sensing,⁵ and thermoluminescence,⁶ which was first introduced by Levine and Palilla.⁷ YVO₄:Eu has the strong red emission lines (⁵D₀-⁷F₂ emission transitions at 614 and 619 nm) by the energy transfer to Eu³⁺ ion following absorption of UV light in the VO₄³⁻ group.⁸ YVO₄:Eu phosphor is recently attracting the attention for application to field emission display(FED) devices due to its sulfur-free composition and fabrication of thin film in relatively low temperature.⁹ Thin films of YVO₄:Eu phosphor have been prepared by a variety of deposition techniques, such as chemical vapor deposition

(CVD),¹⁰ spray pyrolysis¹¹ and sol-gel method.¹² These methods suffer from either a lack of crystallographic orientational control or the incorporation of vanadium-poor or rich nonstoichiometric phase. PLD is an attractive synthetic method for the growth of high-quality crystalline films because it is simple, relatively cheap and reliable technique, which yields high-quality films of various materials. We have investigated on the structural characteristics and photoluminescence(PL) properties of YVO₄:Eu films prepared by PLD which has been known as a unique process providing stoichiometric transfer of target materials.¹⁴

Experimental Section

YVO₄ doped Eu³⁺ was prepared by the typical solid-solid reaction method. The stoichiometric mixture of Y₂O₃ (99.99%), Eu₂O₃ (99.99%) and V₂O₅ (99.99%) was well ground in absolute ethanol, and then heated at 900 °C and 1200 °C for 10 hours and 20 hours in air, respectively, with intermediate grinding and pelleting. Targets for PLD were prepared from YVO₄:Eu powder by cold-pressing followed by sintering for 12 hours at 1200 °C in air. YVO₄:Eu thin films were deposited on Si wafer with typical size of 50 × 50 mm² at room temperature using a frequency tripled Nd:YAG Laser (Quantel, Brilliant B) with 5-ns of pulse width. The laser pulses of 10 Hz were focused onto the rotating target using a quartz lens with 35 cm focal length at a 45° oblique incidence, and energy densities were approximately 2 J/cm². A substrate was set at a distance of 50 mm parallel from the target surface. The films deposited were subsequently post-annealed in air at various temperature.

The structural and phase identification was carried out using an X-ray diffractometer (MacScience Co. MXP-3V) with Cu-K_α radiation. Cross-sectional and plane views were obtained using a scanning electron microscope (SEM) (Hitachi Co. S-4200). The PL spectra were measured using a

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spectrofluorometer (Shimadzu, RF-5301PC) at excitation wavelength of 254 nm. To observe the decay profiles of PL, emission from the sample after excitation by a pulsed laser (Quantel, Minilite II) of 266 nm with pulse width of 5 ns was passed through a monochromator (McPherson 275) with a glass filter in front of the entrance slit. Signals were detected with a photomultiplier tube (Hamamatsu R928) and were stored using a digital storage oscilloscope (LeCroy 9310A).

Results and Discussion

To determine the optimized growth condition for high luminescence of $\text{YVO}_4:\text{Eu}$ film, a systematic study of the effects of annealing temperature and oxygen pressure was carried out. Figure 1 shows the X-ray diffraction (XRD) patterns from films deposited on Si substrate for 4 hrs at 25 °C under 20 mTorr O_2 and that of the polycrystalline powder $\text{YVO}_4:\text{Eu}$ used as a target for a comparison. The films were annealed in air for 6 hr at (a) 550 °C, (b) 950 °C and (c) 1150 °C. The films had excellent adhesion on substrate and showed scratch resistant after post annealation. All the diffraction peaks of thin films can be matched with XRD pattern of the $\text{YVO}_4:\text{Eu}$ powder indexed on tetragonal phase (JCPDS Card 17-341) and no second phase is detected.¹⁰ However, the diffraction peaks due to thin film are a little broader and have a higher degree of shift than the counterparts of $\text{YVO}_4:\text{Eu}$ powder, indicating that the size of the crystalline grains in the film is smaller than that in the powder. The relative intensities in XRD peaks of thin films post-annealed at 550 °C and 950 °C do not show so much difference comparing with those of $\text{YVO}_4:\text{Eu}$ powder, indicating that there is no predominantly preferential growing orientation. The relative intensity of (200) peak is dramatically increased in thin film annealed at 1150 °C. It can be seen clearly that the YVO_4 crystallized with (200) preferred orientation above 950 °C. The preference of (200)-direction in high temperature is well agreed with Korzenskis

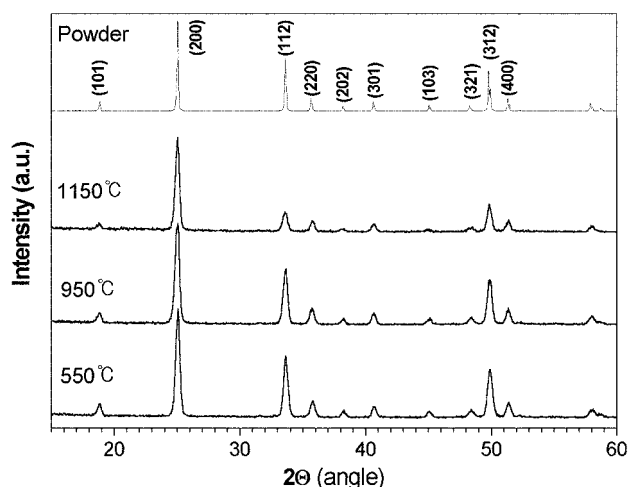


Figure 1. XRD patterns of $\text{Eu}:\text{YVO}_4$ powder and films deposited on silicon substrate at oxygen pressure of 20 mTorr, followed by post annealing at 1150 °C, 950 °C and 550 °C.

result in $\text{Nd}:\text{YVO}_4$ thin film deposition on sapphire substrate.¹³ These changes in film orientation with increase of annealing temperature were reported in deposition of $\text{Y}_2\text{O}_3:\text{Eu}$ film by K. G. Cho *et al.*¹⁴ According to their results, at high temperature, the mobility of thermally activated atom in grain and grain boundary regions disrupts the low energy configuration and allows a transformation in film growth to the best matched orientation with substrate. Therefore, for the $\text{YVO}_4:\text{Eu}$ films on bare silicon, (200) crystalites seem to be well-aligned to the flat silicon surface at high temperature.

The SEM images of films annealed at different temperature (Figure 2) have shown that the grain size increases as annealing temperature increases. The grain size in the $\text{YVO}_4:\text{Eu}$ film annealed at 550 °C is so small that it can not be measured in our SEM image. The grains in film annealed at 950 °C have the size of 100-150 nm, though the boundary between grains is not clearly seen. However, the SEM image of $\text{YVO}_4:\text{Eu}$ film annealed at 1150 °C shows the well-defined grain boundary as well as largely increased grain size of 300-600 nm. This drastic increase in grain size above 950 °C of annealing temperature agrees with XRD result of increase of relative intensity of (200) peak in the same condition although the FWHM of XRD peak has not shown the decrease according to the increase of annealing temperature. This indicates that increase of grain size in SEM

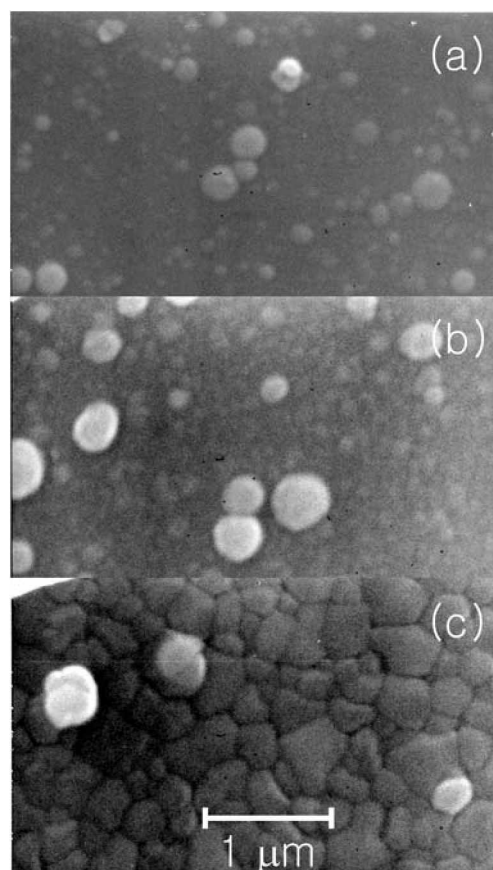


Figure 2. Plane view of SEM images for $\text{Eu}:\text{YVO}_4$ film postannealed at (a) 550 °C (b) 950 °C and (c) 1150 °C.

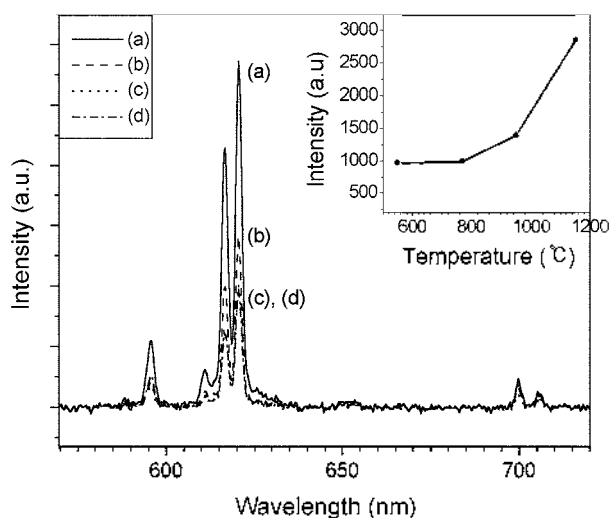


Figure 3. Photoluminescence spectra obtained from 254 nm excitation of $\text{Eu}:\text{YVO}_4$ films grown on silicon substrate at an oxygen pressure of 20 mTorr, followed by post annealing at (a) 1150 °C, (b) 950 °C, (c) 750 °C and (d) 550 °C

image may correspond to the secondary structure not the primary structure in films.

The PL spectra of $\text{YVO}_4:\text{Eu}$ phosphor in Figure 3 show a considerable number of lines between 590 nm and 710 nm, representing the transitions ${}^5\text{D}_0\text{-}{}^7\text{F}_{0,4}$ between the first excited state and the ground multiple of the Eu^{3+} .^{15,16} The crystal field splitting of ${}^5\text{D}_0\text{-}{}^7\text{F}_{1,2,4}$ transitions can be clearly indicated that the film is well-crystallized. The spectra are dominated by the emission from mainly ${}^5\text{D}_0\text{-}{}^7\text{F}_{2,4}$ forced electric-dipole transitions for which high intensities are a consequence of the absence of an inversion symmetry at the Eu^{3+} lattice site.^{17,18} Other contributions of weaker importance are the ${}^5\text{D}_0\text{-}{}^7\text{F}_{1,3}$ magnetic dipole transitions. While the pattern of PL spectra of films do not show dramatic differences with annealing temperature, the intensity of PL in films has some difference with annealing temperature. The PL spectra show the sudden increase in intensity at an annealing temperature of 1150 °C, whereas the intensity shows a slow increase from 550 °C to 950 °C of annealing temperature as XRD patterns and SEM images. Since grain boundaries may be the sources of electron trapping and dissipation of light generated inside the film, reducing the PL brightness, the films with less grain boundaries exhibit superior PL properties. As shown in Figure 2, the density of grain boundaries in the $\text{YVO}_4:\text{Eu}$ films grown at higher temperature is smaller than in the $\text{YVO}_4:\text{Eu}$ films grown at lower temperature. The drastic increase of PL brightness of $\text{YVO}_4:\text{Eu}$ film deposited at 1150 °C is believed to result from improved crystallinity and enhanced grain size of film.

Figure 4 shows the PL intensity of $\text{Eu}:\text{YVO}_4$ films as a function of oxygen growth pressure. As shown in Figure 4, the PL intensity of $\text{Eu}:\text{YVO}_4$ films increases as the oxygen growth pressure increases to 200 mTorr but shows no change in films grown in above 200 mTorr of oxygen pressure. The films grown in lower oxygen pressure than 200 mTorr show the bright reflection and good adhesion on

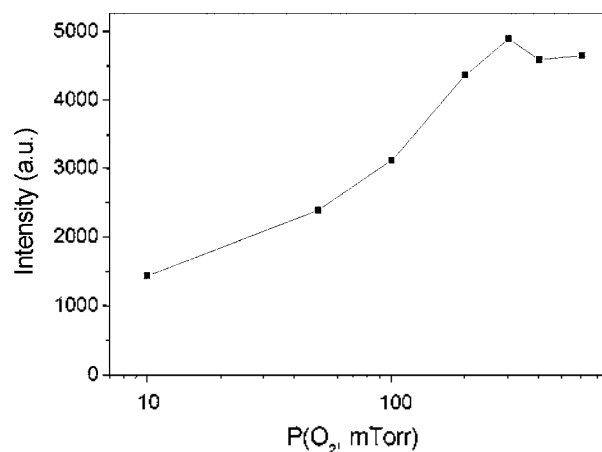


Figure 4. Photoluminescence intensity of $\text{YVO}_4:\text{Eu}^{3+}$ films as a function of oxygen pressure. The films were deposited on silicon substrate during 1 hr and the post annealing temperature was 1150 °C for all of the films.

Si substrate while the films grown in above 200 mTorr of oxygen pressure are easily scratched and have the powder-like surface morphology. According to the result of S. L. Jones *et al.*,¹⁹ the phosphor films grown in higher oxygen pressure have rougher surfaces than films grown in lower oxygen pressure. The increase in roughness with increasing growth pressure is attributed to enhanced particulate formation in the laser induced plume which is a typical characteristic of high pressure laser ablation.²⁰ The reduced internal reflections caused by rough surfaces probably bring about improvement of PL performance in $\text{YVO}_4:\text{Eu}$ films grown at higher oxygen pressure.

In $\text{YVO}_4:\text{Eu}$, ultraviolet radiation excites the host lattice and then transfers to the Eu^{3+} ion of ${}^5\text{L}_J$ or ${}^5\text{G}_J$ level. These highly excited states of Eu^{3+} lead to the ${}^5\text{D}_J$ level by means of fast nonradiative relaxation processes at room temperature. The static PL spectrum of Eu^{3+} is dominated by the transition from ${}^5\text{D}_0$ which is the lowest state among ${}^5\text{D}_J$ states. The nonradiative transition from the ${}^5\text{D}_1$ level to the ${}^5\text{D}_0$ level is a phenomenon well-known as the cross relaxation.²² Due to similar energy differences of ${}^5\text{D}_1\text{-}{}^5\text{D}_0$ (1734 cm^{-1}) and ${}^7\text{F}_3\text{-}{}^7\text{F}_0$ (1857 cm^{-1}),²³ the energy exchange may occur between the excited Eu^{3+} (${}^5\text{D}_1$) ion and the adjacent ground state Eu^{3+} (${}^7\text{F}_0$) ion. Therefore, the decay time of luminescence from ${}^5\text{D}_1$ level is exactly matched with the rise time of luminescence of ${}^5\text{D}_0$ level as reported in Riwoztk's result.²⁴ It suggests that these luminescence life time of ${}^5\text{D}_0$ and ${}^5\text{D}_1$ level can be used as a good parameter to evaluate the stoichiometric transfer of $\text{YVO}_4:\text{Eu}$ phosphor in thin film deposition. Figure 5 shows the PL decay profiles of the emission from ${}^5\text{D}_1$ to ${}^7\text{F}_3$ at 538.3 nm after irradiation with a laser pulse of 266 nm of $\text{YVO}_4:\text{Eu}$ powder according to variation with Eu^{3+} contents and thin film deposited by PLD. As shown in Figure 5, the PL decay of ${}^5\text{D}_1$ level of $\text{YVO}_4:\text{Eu}$ powder becomes faster with increase of concentration of Eu^{3+} ion. The inset in Figure 5 depicts the fitted exponential-decay time of ${}^5\text{D}_1$ level. The decay time of $\text{YVO}_4:\text{Eu}$ level is monotonically decreased from 8.44 μs to

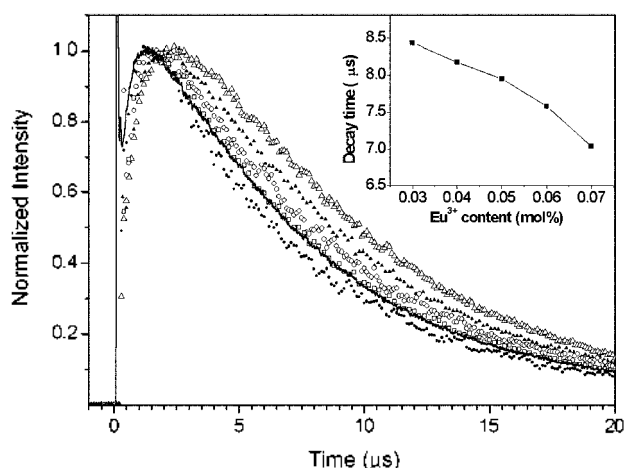


Figure 5. Luminescence decay profiles from 5D_1 state of Eu^{3+} of $\text{YVO}_4:\text{Eu}$ powders and films (solid line) observed at 538.3 nm followed by excitation at 266 nm under room temperature. The europium concentrations of powder were as follows. (1) open triangle: 3.0 mol%; (2) filled triangle: 4.0 mol%; (3) open circle: 5.0 mol%; (4) open square: 6.0 mol%; (5) filled circle: 7.0 mol%. The inset depicts the fitted decay time constants of $\text{YVO}_4:\text{Eu}$ powder as a function of Eu^{3+} concentration.

7.04 μs as the concentration of Eu^{3+} ion increases from 3.0 mol% to 7.0 mol%. Although it has the slight difference with 6.6 μs of 5 mol% $\text{YVO}_4:\text{Eu}$ nanocrystalline powder in Riwozki's result, it shows the great concentration dependency. The decay time of 5D_1 level of thin film deposited 10 mTorr and 100 mTorr of oxygen pressure is 7.47 μs and 7.43 μs , respectively, which are slightly shorter than 7.95 μs of 5 mol% $\text{YVO}_4:\text{Eu}$ powder used as target material for deposition. This represents that the Eu^{3+} get slightly richer in deposition process than that of $\text{YVO}_4:\text{Eu}$ powder.

The use of short laser pulses in PLD is more likely to achieve congruent ablation that allows PLD to preserve stoichiometry during mass transfer from the target to the thin film. Immediately after the laser irradiation, the plume which consists of a mixture of energetic species including atoms and molecules, rapidly expands into the vacuum from the target surface to form a jet with hydrodynamic flow characteristics. The richness of Eu^{3+} in thin film might be caused by more rapid decrease of lighter species with small momentum due to the collisions with the background gas as the plume expands from target. Though the specific effects of target-to-substrate distance and ambient pressure are expected on these mass discrimination in plume expansion, it could not be observed in our experimental condition.

In summary, it has been shown that the surface morphology and hence the luminescence properties can be altered significantly by changing the PLD growth conditions. A post-annealing treatment led to a significant improvement in

brightness of $\text{YVO}_4:\text{Eu}$ films. Though the post-annealing at 1150 $^\circ\text{C}$ in this study is definitely concern for flat panel manufacturers that currently use low temperature substrates, the main purpose of present work is understanding the conditions required to produce efficient phosphor films and the further study will be possible to find the film fabrication process at low temperature for flat panel display with combination with modified surface and substrate.

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