Pulsed-Laser Deposition of YVO₄:Eu Phosphor Thin-Films for Low Temperature Fabrication

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Received April 27, 2001

In an early development of low-voltage cathodoluminescent (CL) phosphors for applications to field emission display (FED) devices, the cathode-ray tube (CRT) phosphors have readily been tested as candidates. In case of the red phosphor materials, unfortunately, Y_2O_2S:Eu which is used as the red primary in the CRT has known to be degraded under electron bombardments with high current densities and contaminate the cold cathodes, resulting in a fatal damage to FED devices.[1]

The oxide based thin-film phosphors are highly attractive in use of the FED devices because of advantages such as higher lateral resolution from smaller grains, better thermal and mechanical stability, and reduced outgassing over conventional powder phosphors.[2] Among the oxide phosphors, Y_2O_3:Eu is currently one of the leading red phosphor materials for FEDs.[3] Y_2O_3:Eu films have been grown using various deposition techniques.[4-9] However, because of its high melting point of about 2400 °C, Y_2O_3:Eu thin films require a post-annealing process at high temperatures above 1000 °C to crystallize the deposits.[7-10] Therefore, the high temperature process is inevitable in order to obtain high efficient and bright Y_2O_3:Eu thin-film phosphors and Y_2O_3:Eu films had been grown only on the heat-resistant substrates such as Si wafer,[7,8] Ni based alloy[9] and sapphire plate.[10] However, the annealing at high temperature is definitely a concern for fabrication of current FED devices which adapt low temperature glass substrates. By this reason, YVO₄:Eu with the relatively low melting point is re-interested as a red phosphor precursor for the thin film process at low temperature.

Bulk YVO₄ has been widely used as a host material for phosphor of lanthanide ions since high luminescence quantum yields are observed for the $f - f$ transitions.[11] YVO₄:Eu shows relatively strong red emission lines ($^5D_0$-$^7F_2$ emission transitions at 614 and 619 nm) by the energy transfer to Eu^{3+} ion following absorption of UV light in the VO_4^{3-} group.[12] However, there has been no report on the growth of YVO₄ films by any of the physical vapor deposition techniques, except for chemical vapor deposition (CVD).[13] We have investigated on the structural characteristics and photoluminescence (PL) properties of YVO₄:Eu films prepared by

PLD which is a unique process providing stoichiometric transfer of target materials.[14]

Experimental Section

YVO₄ doped Eu^{3+} concentration at 5 mol% was prepared by the typical solid reaction method. The stoichiometric mixture of Y_2O_3 (99.99%), Eu_2O_3 (99.99%) and V_2O_5 (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 under total pressure of 2×10^{-6} Torr at room temperature using a frequency quadrupled Nd:YAG Laser (Continuum Co, Minilite II) with 5 ns of pulse width. The laser pulse of 10 Hz was focused onto the rotating target using a quartz lens with 35 cm focal length to give laser fluence of 80 mJ/cm². Corning glass coated with 35 nm-thick indium-tin oxide(ITO) and fused silica were used as substrates. A substrate-target distance was 2.0 cm. The films deposited were subsequently post-annealed in air at 500 °C for 24 hours.

The structural and phase identification were 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 spectrofluorometer (Shimadsu, RF-5301PC) at excitation wavelength of 254 nm. To observe the decay profiles of PL, the emission from the sample after excitation by a pulsed laser of 266 nm 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

Figure 1 shows the SEM micrographs of YVO₄:Eu film grown on ITO glass substrate at room temperature during 30 minutes of irradiance time. The cross-sectional view of Figure 1(a) shows that the film thickness is about 180 nm

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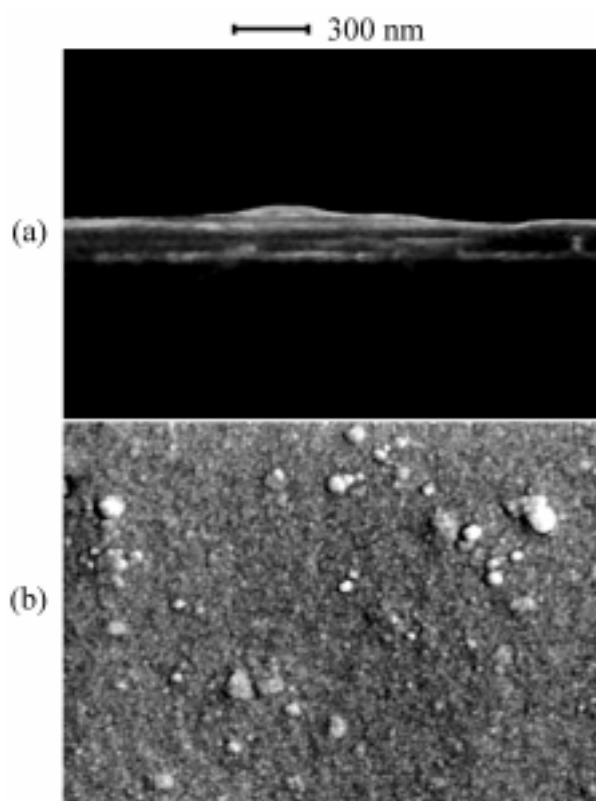
Figure 1. Cross-sectional (a) and plane view (b) of SEM images for Eu:YVO$_4$ film grown on ITO-coated glass substrate at room temperature.

and the deposition rate corresponds to about 60 Å/min in this condition. As can be seen from the surface micrograph, the film consists of ultra-fine grains in size from about 10 to 30 nm. The films had excellent adhesion on substrate and showed scratch resistant after post annealation at 500 °C.

The X-ray diffraction (XRD) patterns for the films post-annealed at 500 °C on ITO glass and fused silica substrates
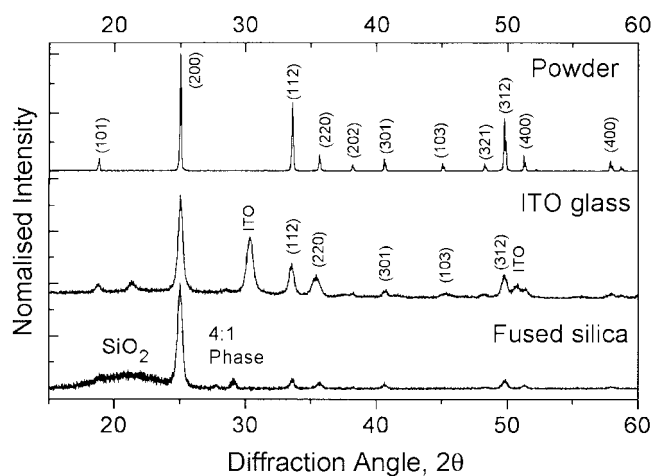
are shown in Figure 2. Compared with XRD pattern for polycrystalline YVO$_4$:Eu phosphor powder used as a target, most peaks in both films are broadened due to small particle size and could be indexed on tetragonal YVO$_4$:Eu phase. While the film grown on fused silica substrate shows relatively well-preferred orientation of (200) plane, the film grown on ITO glass exhibits nearly the same relative intensity as the polycrystalline XRD pattern, indicating that there is no predominantly preferential growing orientation at the present film preparation condition. And also small diffraction peaks are observed at 28.6° and 29.2° for the film grown on fused silica substrate, which might be due to the formation of Y$_8$V$_2$O$_{17}$ (4 : 1 phase) secondary phase.[13]

The PL spectra of YVO$_4$:Eu phosphor in Figure 3 show a considerable number of lines between 530 and 710 nm, representing the transitions $^5D_{0,1}$-^7F_J between the first excited states and the ground multiple of the Eu^{3+}. While the PL spectra of films do not show dramatic differences with substrates, the intensity of PL in films is relatively weak compared with the powder. Considering the piping effect in phosphor films and the detection of only one side emission on transparent substrates used in this study, the total efficiency of the luminescence in films must be much stronger than the PL intensity measured. This apparent low brightness can be enhanced by the increase of roughness of surface[9] and film thickness. The $^5D_0$-^7F_J emission is very suitable to survey the environmental effects on the sites of Eu^{3+} ion in a host lattice without inversion symmetry such as YVO$_4$.[15] While the $^5D_0$-$^7F_4$ transition is sensitive to long-range environmental effects, the $^5D_0$-$^7F_2$ transition which originates from interactions with neighbors is hypersensitive to, especially short-range, environmental effects. However, the $^5D_0$-$^7F_1$, the allowed magnetic-dipole transition, is not affected by the Eu^{3+} ion so that it is usually utilized as an internal standard. The similar intensity ratios of $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_4$ transitions to $^5D_0$-$^7F_1$ transition in PL spectrum of

Figure 2. XRD patterns of Eu:YVO$_4$ powder (a) and films deposited on ITO glass (b) and quartz plate (c) followed by annealing at 500 °C during 24 hours.
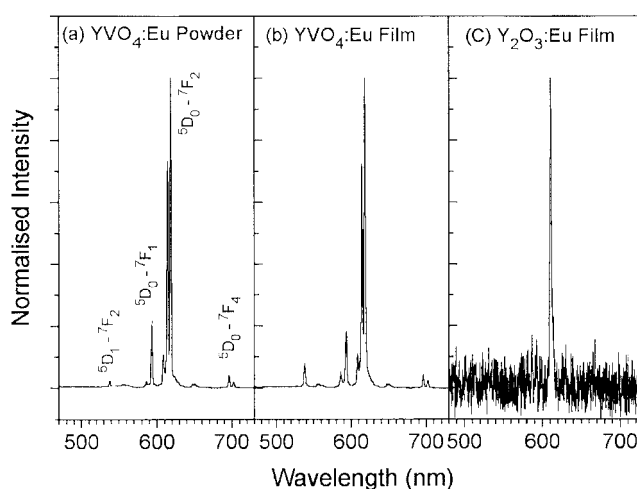

Figure 3. PL spectra obtained from 254 nm excitation of Eu:YVO$_4$ powder (a) and film (b) and Y$_2$O$_3$:Eu film (c) of the commercial product. Both films were deposited on ITO glass at room temperature followed by annealing at 500 °C during 24 hours.

Notes

Bull. Korean Chem. Soc. **2001**, Vol. 22, No. 8 923

YVO$_4$:Eu represent that Eu^{3+} ions are occupied in yttrium sites of YVO$_4$ lattice and the long-range environments of Eu^{3+} ions in the film are not much different from powder. This indicates that YVO$_4$:Eu film deposited by PLD is well crystallized within small grain sizes of 10-30 nm even at low post-annealing temperature. However, PL of Y$_2$O$_3$:Eu film deposited on ITO glass in the same PLD condition could not be observed by the naked eyes even in a dark room at this post-annealing temperature of 500 °C and only the strongest transition line of 611 nm were measured with some difficulty as shown in Figure 3(c).

In YVO$_4$:Eu, ultraviolet radiation excites the host lattice and then transfers to the Eu^{3+} ion of ^{5}L$_J$ or ^{5}G$_J$ level. These highly excited states of Eu^{3+} lead to the ^{5}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}D$_0$ which is the lowest state among ^{5}D$_J$ states. Figure 4 shows the PL decay profiles of the main emission line (^{5}D$_0$-^{7}F$_2$, 619 nm) and the transition of ^{5}D$_1$-^{7}F$_1$ (538 nm) after irradiation with a laser pulse of 266 nm. The decay of the main emission lines of YVO$_4$:Eu shows slightly non-exponential behavior. The decay times (τ_{10}) to 10% of its initial value after excitation are 600 and 420 μs in films on ITO glass and fused silica substrate, respectively, which are much shorter than 1300 μs of powder. According to Stoffers *et al.*, the phosphors with the fast decay time may overcome ground state depletion and can lead to a brighter FED which is operated at low voltages and high current densities.[16] The faster decay rate allows for the activator to be excited several times by recycling during an excitation pulse. Compared with decay times of 900 μs[7] and 2.5 ms of Y$_2$O$_3$:Eu in film and powder, respectively, YVO$_4$:Eu shows less saturation behavior in CL excitation with high current density.

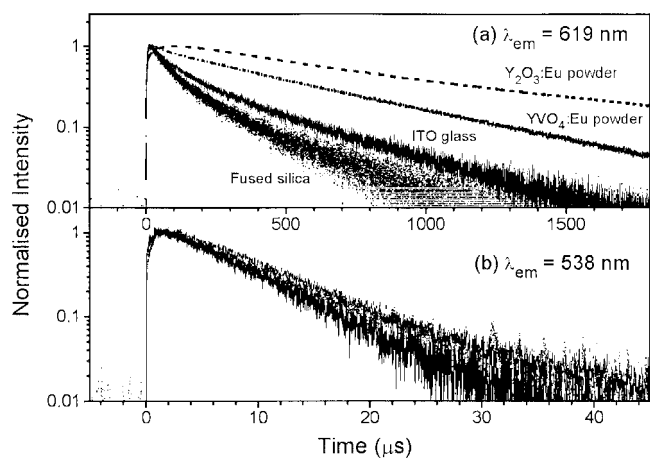The nonradiative transition from the ^{5}D$_1$ level to the ^{5}D$_0$

level is a phenomenon well-known as the cross relaxation,[12] which is dependent on the concentration of activator in the case of high doping level. Due to similar energy differences of ^{5}D$_1$-^{5}D$_0$ (1734 cm^{-1}) and ^{7}F$_3$-^{7}F$_0$ (1857 cm^{-1}),[17] the energy exchange may occur between the excited Eu^{3+} (^{5}D$_1$) ion and the adjacent ground state Eu^{3+} (^{7}F$_0$) ion. Therefore, the higher level emission is quenched in favor of the lower energy level emission, resulting in the concentration-dependent life time of ^{5}D$_1$ state. The PL decay from ^{5}D$_1$ level, which is well fitted to exponential decay, does not show a significant difference regarding the phase of YVO$_4$:Eu phosphor. The fitted exponential decay times of 7.1 ± 0.2 ms are well each consistent in their error range, indicating the similar extents of cross relaxation from the ^{5}D$_1$ level. This suggests that the contents of Eu^{3+} are not much different in film and powder, showing the advantage of PLD for the control of chemical composition in film growth by congruent evaporation.

This note represents the growth of the YVO$_4$:Eu phosphor thin-film. YVO$_4$:Eu phosphor films were deposited on ITO coated glass and fused silica substrate using a pulsed laser deposition technique at room temperature. The deposited thin films are well crystallized after post-annealing at temperature as low as 500 °C and reveal the PL characteristics with a faster decay time of the main transition line compared with powder system, which will be of benefit to luminescence saturation behavior at CL excitation. These results present that red light emitting YVO$_4$:Eu thin-film phosphor is a promising candidate for low temperature fabrication process for the FED devices.

Figure 4. Luminescence decay profiles from ^{5}D$_1$ state of Eu^{3+} observed at 538 nm (a) and ^{5}D$_0$ state of Eu^{3+} observed at 619 nm (b) followed by excitation at 266 nm under room temperature. (1) —— : Eu:YVO$_4$ film on ITO glass; (2) ······ : Eu:YVO$_4$ film on quartz plate; (3) – · – : Eu:YVO$_4$ powder; (4) ——: Eu:Y$_2$O$_3$ powder. The decay profile of Eu:Y$_2$O$_3$ powder is not shown in (b).

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