UV cathodoluminescence of Gd³⁺ doped and Gd³⁺–Pr³⁺ co-doped YAlO₃ epitaxial thin films

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Thin films of YAlO₃:Gd³⁺ and YAlO₃:Gd³⁺–Pr³⁺ were prepared on LaAlO₃ (001) single crystal substrates by pulsed laser deposition (PLD). Both films were grown epitaxially and their surfaces were uniformly smooth. Under UV excitation at 216 nm, YAlO₃:Gd³⁺ film did not show any intense photoluminescence (PL); on the other hand, YAlO₃:Gd³⁺–Pr³⁺ film showed intense Gd³⁺ PL at 314 nm through Pr³⁺ 4f–5d absorption. Under electron irradiation with acceleration of 2.00 kV, both films showed UV cathodoluminescence (CL) from Gd³⁺ ions. In contrast to PL, the CL intensity of the YAlO₃:Gd³⁺ film was four times greater than that of the YAlO₃:Gd³⁺–Pr³⁺ film. The PL excitation spectrum of YAlO₃:Gd³⁺ in vacuum UV region revealed the presence of an intense excitation band at 155 nm assignable to YAlO₃ host absorption. This observation implied that the energy of accelerated electrons was absorbed by the host and then transferred to Gd³⁺. Pr³⁺ co-doping was found to weaken the Gd³⁺ emission in CL because the excitation energy absorbed by the host was transferred to not only Gd³⁺ but also Pr³⁺ accompanying visible emission and nonradiative transition in Pr³⁺.

1 Introduction

Some UV emitting perovskite-type oxide phosphors such as $(Y_{1-x}Lu_x)AlO_3:Ce^{3+}$, $(Y_{1-x}Lu_x)AlO_3:Pr^{3+}$, and $YAlO_3:Gd^{3+}$ have been reported in the form of single crystals or powders [1–11]. Ce^{3+} and Pr^{3+} show a broad UV emission peak attributed to 5d–4f transition. Because their emission decay time is as short as approximately 10 ns, Ce^{3+} and Pr^{3+} doped perovskite-type oxide phosphors were examined to use as a scintillator [1–9]. On the other hand, Gd^{3+} shows a sharp UV emission attributed to 4f–4f transition from $^6P_{7/2}$ to $^8S_{7/2}$ ground level in Gd^{3+} [12, 13]. Using the sharp UV emission, some applications such as a phototherapy lamp for skin diseases and a transilluminator for DNA analysis are anticipated [14, 15]. Because the studies of these phosphors have been mainly conducted in the form of single crystals or powders [1–11], their thin films have not been extensively studied yet in terms of both film growth and optical evaluation.

Perovskite-type oxides frequently form high quality thin films on perovskite-type substrates. Actually, the growth of high quality phosphor thin films such as $AHfO_3:Tm^{3+}$, $ATiO_3:Pr^{3+}$, and $ASnO_3:Tb^{3+}$ on $SrTiO_3$ substrates has been reported along with their intense visible photoluminescence (PL) [16–18]. Because oxide phosphors have excellent chemical stability, thin films of the perovskite-type oxide phosphors are suitable for some application to thin-film-type optoelectronic devices.

The PL of Gd^{3+} doped $YAlO_3$ was recently examined and Pr^{3+} co-doping was found to enhance the UV PL of Gd^{3+} [10, 11, 19]. To develop surface emitting devices or other optoelectronic application, the examinations of cathodoluminescence (CL), as well as PL, of the Gd^{3+} doped $YAlO_3$ phosphors are important. Although Gd^{3+} doped $YAlO_3$ is a promising phosphor in PL, no investigation on its CL has been reported yet. In this study,
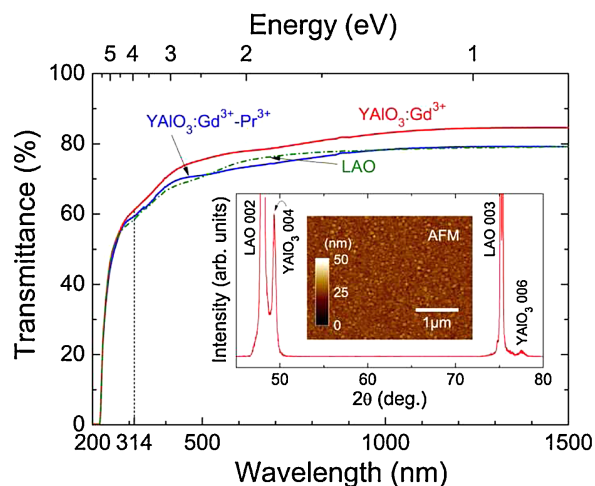
fine thin films of YAlO$_3$:Gd^{3+} and YAlO$_3$:Gd^{3+}–Pr^{3+} were grown by pulsed laser deposition (PLD), and their UV CL properties were evaluated for future application to Gd^{3+} UV emitting devices.

2 Experiments YAlO$_3$:Gd^{3+} and YAlO$_3$:Gd^{3+}–Pr^{3+} films were deposited on LaAlO$_3$ (LAO) (001) pseudocubic single crystal substrates by PLD. Polycrystalline YAlO$_3$:Gd^{3+} and YAlO$_3$:Gd^{3+}–Pr^{3+} sintered disks with the nominal compositions of (Y$_{0.97}$Gd$_{0.03}$)AlO$_3$ and (Y$_{0.94}$Gd$_{0.03}$Pr$_{0.03}$)AlO$_3$, respectively, were used as targets. The deposited thin films were annealed at 1000 °C in air to improve crystallinity and luminescent intensities. Detailed PLD and annealing conditions are listed in Table 1. X-ray diffraction (XRD) patterns of the films were measured by an X-ray diffractometer (Rigaku, RINT 2500), and surface morphology of the films was observed using an AFM (Digital Instruments, Nanoscope III). The concentrations of Gd^{3+} and Pr^{3+} in the films were analyzed by XPS (SHIMADZU/KRATOS, AXIS-NOVA) evaluating Gd 3d$_{5/2}$ and Pr 3d$_{5/2}$ peak intensities. Transmission spectra and PL/PL excitation (PLE) spectra were measured using an UV/Vis/NIR spectrophotometer (Jasco, V-570) and a spectrofluorometer (Jasco, FP-6500), respectively. A PLE spectrum in vacuum UV (VUV) region was measured using a polycrystalline YAlO$_3$:Gd^{3+} disk at the beam line BL-7B of UVSOR in the Institute for Molecular Science. CL spectra of the films were measured using a field emitter with a gate electrode as an electron source and a spectrofluorometer (Jasco, FP-6500) with an optical fiber. In the CL measurements, the acceleration voltage in the electron emitter was varied from 0.00 to 2.00 kV.

3 Results and discussion Epitaxial growth of the films was confirmed by XRD and reflected high-energy electron diffraction (RHEED). An XRD pattern of the YAlO$_3$:Gd^{3+} film is shown in the inset of Fig. 1. The XRD pattern of the YAlO$_3$:Gd^{3+}–Pr^{3+} film, which is not displayed in the inset, was nearly the same. Strong peaks assigned to (00l) planes were observed indicating the

Table 1 PLD and annealing conditions.

PLD conditions	
target	(Y$_{0.94}$Gd$_{0.03}$Pr$_{0.03}$)AlO$_3$
	(Y$_{0.97}$Gd$_{0.03}$)AlO$_3$
substrate	LaAlO$_3$ (001) single crystal
laser source	ArF excimer (193 nm)
laser fluence	~1.2 Jcm^{-2}pulse^{-1}
laser frequency	16 Hz
O$_2$ partial pressure	0.1 Pa
substrate temperature	740 °C

annealing conditions	
atmosphere	air
temperature	1000 °C
duration	1 h

Figure 1 Transmission spectra of YAlO$_3$:Gd^{3+} and YAlO$_3$:Gd^{3+}–Pr^{3+} thin films. XRD pattern of orthorhombic YAlO$_3$:Gd^{3+} thin film is shown in the inset along with the AFM image of its surface.

epitaxial growth of the films. Small lattice mismatch between YAlO$_3$ and LAO (2.2%) are responsible for the epitaxial growth. Streaky patterns observed by RHEED demonstrated a high crystal quality of the epitaxial films. The dopant concentrations in the film examined by XPS were Gd 3.9% for the YAlO$_3$:Gd^{3+} film and Gd 3.9%/Pr 3.2% for the YAlO$_3$:Gd^{3+}–Pr^{3+} film, which were almost the same with those in the targets. Transmission spectra of thin films and substrate are shown in Fig. 1. Drastic transmittance drop at 220 nm was ascribed to the fundamental absorption edge of LAO [20]. Transmittance of a LAO substrate at 314 nm was found to be high (>60%) enough to transmit Gd^{3+} emission. The transmittances of both films on LAO substrates were as high as that of the LAO substrate, demonstrating their high transmittances. Film thicknesses were estimated to be approximately 220 nm by interference in the transmission spectra. Flat and smooth surface of the YAlO$_3$:Gd^{3+} film was observed in the AFM image shown in insets. The surface of the YAlO$_3$:Gd^{3+}–Pr^{3+} film was also as fine as that of the YAlO$_3$:Gd^{3+} one.
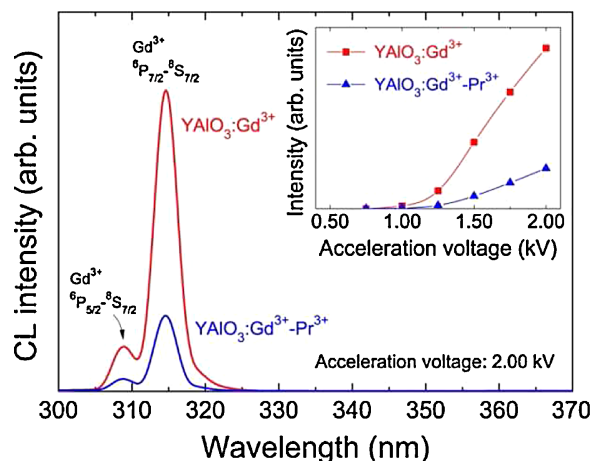
Figure 2 shows PL and PLE spectra of YAlO$_3$:Gd^{3+}, YAlO$_3$:Gd^{3+}–Pr^{3+} films, and a PLE spectrum of YAlO$_3$:Gd^{3+} bulk in VUV region. A sharp emission peak, which was attributed to the $^6P_{7/2}$–$^8S_{7/2}$ transition in Gd^{3+}, was observed at 314 nm in both PL spectra. Another small emission peak attributed to the $^6P_{5/2}$–$^8S_{7/2}$ was also observed at 308 nm [12, 13]. In the PLE spectrum of the YAlO$_3$:Gd^{3+}–Pr^{3+} film, an intense broad excitation band was observed around 216 nm, which was assigned to the 4f–5d transition in Pr^{3+} [1-5]. The intense excitation band indicated the excitation energy absorbed by Pr^{3+} was transferred from Pr^{3+} to Gd^{3+}, resulting in the distinctive Gd^{3+} emission at 314 nm. On the other hand, no obvious excitation band was observed in the PLE spectrum of the YAlO$_3$:Gd^{3+} film in the wavelength region above 200 nm. Accordingly, the Gd^{3+} emission intensity was very weak in

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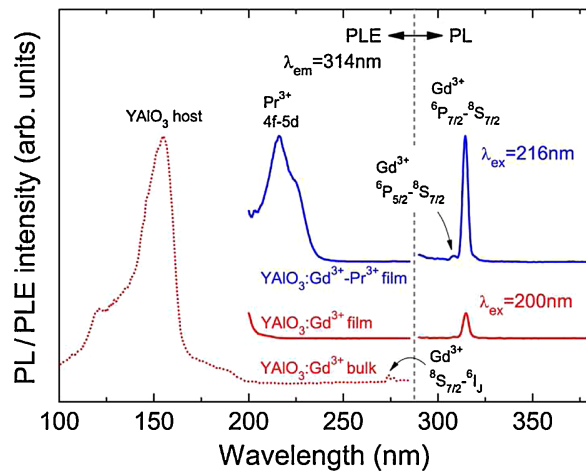
Figure 2 PL/PLE spectra of $YAlO_3$:Gd^{3+} and $YAlO_3$:Gd^{3+}–Pr^{3+}. Solid lines exhibit spectra of $YAlO_3$:Gd^{3+} and $YAlO_3$:Gd^{3+}–Pr^{3+} thin films. The dotted line exhibits spectrum of $YAlO_3$:Gd^{3+} bulk.

the $YAlO_3$:Gd^{3+} film, as far as the PL spectrum was measured using a conventional spectrofluorometer with a xenon lamp. The PLE spectrum of a $YAlO_3$:Gd^{3+} bulk in the VUV region revealed that an intense excitation band was located at 155 nm (8.0 eV). The energy of the excitation band corresponded to the band gap energy of $YAlO_3$[21]. Accordingly, it was found that excitation of $YAlO_3$ host by VUV irradiation led to the intense Gd^{3+} emission even in Gd^{3+} single doped $YAlO_3$.
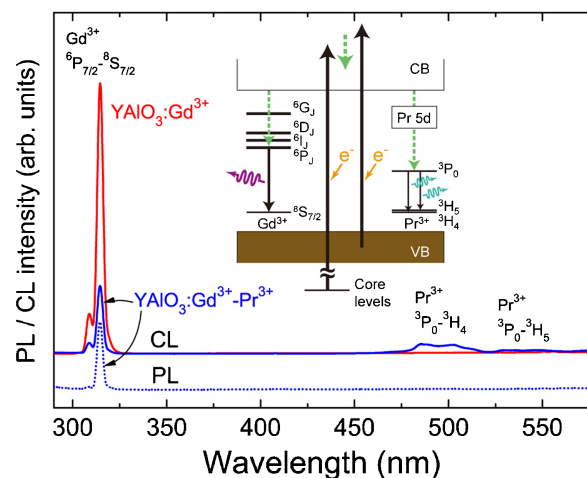
Figure 3 shows CL spectra of $YAlO_3$:Gd^{3+} and $YAlO_3$:Gd^{3+}–Pr^{3+} thin films at electron acceleration voltage of 2.00 kV. An intense UV CL peak attributed to the Gd^{3+} $^6P_{7/2}$–$^8S_{7/2}$ transition was observed at 314 nm. Another CL peak attributed to $^6P_{5/2}$–$^8S_{7/2}$ was observed more clearly than that in the PL spectra. Because the energy of accelerated electrons is as high as a few keV, the excitation energy by electron irradiation in CL is first absorbed by the $YAlO_3$ host. Therefore, the observation of the intense Gd^{3+} CL peak suggested that the energy transfer from the $YAlO_3$ host to Gd^{3+} occurred smoothly, which is similar to the intense PL in the $YAlO_3$:Gd^{3+} bulk observed under VUV excitation. Inset of Fig. 3 shows acceleration voltage dependence of the CL intensity at 314 nm. The films started to exhibit the Gd^{3+} CL peak at the acceleration voltage above 0.75 kV. With increasing the acceleration voltage, the CL intensity of the films increased. At a 2 kV acceleration, the CL intensity of the $YAlO_3$:Gd^{3+} film was four times greater than that of the $YAlO_3$:Gd^{3+}–Pr^{3+} film.

In the PL spectra, the $YAlO_3$:Gd^{3+}–Pr^{3+} film gave more intense Gd^{3+} emission than the $YAlO_3$:Gd^{3+} film. On the contrary, in the CL spectra, the $YAlO_3$:Gd^{3+} film showed more intense Gd^{3+} emission than the $YAlO_3$:Gd^{3+}–Pr^{3+} film. To understand the contrast between PL and CL, the CL spectra of these films are compared, along with the PL spectrum of the $YAlO_3$:Gd^{3+}–Pr^{3+} film, in the wide wavelength range as shown in Fig. 4. The intensities of the PL spectrum for the $YAlO_3$:Gd^{3+}–Pr^{3+} film were normalized as the PL intensity of Gd^{3+} emission agreed with its CL intensity. In CL originating from $YAlO_3$ host excitation, the $YAlO_3$:Gd^{3+} film showed only Gd^{3+} peaks in UV region, whereas the $YAlO_3$:Gd^{3+}–Pr^{3+} film showed not only the Gd^{3+} peaks but also Pr^{3+} peaks in visible region. The CL peaks at 490 and 540 nm were assigned to $^3P_0$–$^3H_4$ and $^3P_0$–$^3H_5$ transitions in Pr^{3+}, respectively [22]. In PL originating from Pr^{3+} 4f–5d excitation, the $YAlO_3$:Gd^{3+}–Pr^{3+} film showed no peaks in visible region but the Gd^{3+} peaks in UV region. The observation of the Pr^{3+} visible emissions in CL revealed that the excitation energy absorbed by the host was transferred to not only Gd^{3+} but also Pr^{3+}, and the energy transfer from Pr^{3+} to Gd^{3+} was not dominant in contrast to PL. The contrast of Gd^{3+} emission intensity is probably attributed to not simply the difference of excitation source, PL or CL, but also the difference of excitation target, Pr^{3+} 4f–5d or host excitation.

Figure 3 CL spectra of $YAlO_3$:Gd^{3+} and $YAlO_3$:Gd^{3+}–Pr^{3+} thin films. Inset shows acceleration voltage dependence of CL intensity at 314 nm.

Figure 4 CL spectrum of $YAlO_3$:Gd^{3+} and CL and PL spectra of $YAlO_3$:Gd^{3+}–Pr^{3+} thin films in UV and visible region. Inset shows CL mechanisms of $YAlO_3$:Gd^{3+}–Pr^{3+}.

Furthermore, because concentration quenching of Pr^{3+} emissions in YAlO$_3$:Pr^{3+} has been reported to occur at Pr^{3+} concentration over 1% [23], Pr^{3+} co-doping at 3% in the YAlO$_3$:Gd^{3+}–Pr^{3+} film implies the presence of non-radiative transitions as well as visible f–f transitions in CL. Although further studies are necessary to analyze the detailed PL and CL mechanisms, it became clear that Pr^{3+} co-doping was ineffective in CL and decreased the overall efficiency of Gd^{3+} emission. Namely, the intense Gd^{3+} CL peaks were observed in Gd^{3+} single doped YAlO$_3$ because the excitation energy absorbed by the host was concentrated in only Gd^{3+}.

4 Conclusion Epitaxial thin films of YAlO$_3$:Gd^{3+} and YAlO$_3$:Gd^{3+}–Pr^{3+} were grown on LAO (001) substrate by PLD. Regardless of dopants, the transmittance of the films was high and their surface morphology was uniformly smooth. In the CL measurements, YAlO$_3$:Gd^{3+} was found to give an intense Gd^{3+} emission at 314 nm assigned to ^6P_J–$^8S_{7/2}$ transition. Because Gd^{3+}–Pr^{3+} co-doping caused the energy leakage from the host to Pr^{3+}, it was concluded that Gd^{3+} single doping was appropriate in CL to transfer the absorbed energy to Gd^{3+} only.

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