

Photoluminescence and Electroluminescence of $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ Thin Film

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A novel electroluminescence oxide phosphor $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ has been prepared by electron beam evaporation. The emission peaks of photoluminescence lie at 390 nm and a shoulder at 440 nm. However, the electroluminescence of the $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ thin film have four emission peaks at 358 nm, 390 nm, 439 nm and 510 nm, respectively. The optical absorption of $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ thin film and the photoluminescence of composite materials with various ratios of $\text{Ga}_2\text{O}_3/(\text{Gd}_2\text{O}_3+\text{Ga}_2\text{O}_3)$ have also been described to investigate the origin of emission of photoluminescence and electroluminescence.

KEYWORDS: thin film electroluminescence, photoluminescence, $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$

Alternating-current thin film electroluminescence (ACTFEL) devices have been successfully applied in bright monochrome and multicolor flat panel displays for several years.^{1,2)} A bright blue electroluminescence (EL), once a limit of TFEL, has been obtained by Sun *et al.*,³⁾ and Park and co-workers group^{4–6)} recently using SrS:Cu, Ag as emitting materials, which will make the blue emission devices into production in recently years. However, they used the molecular beam epitaxy (MBE) to prepare the phosphor film. And due to the sulphur vacancy and instability of sulphur phosphor the annealing temperature is very high. Therefore it is difficult to obtain the large area TFEL devices using this method on the ordinary glass with indium tin oxide (ITO).

A lot of works have concentrated on oxide phosphors. Minami and co-workers^{7–9)} have obtained multicolor-emitting phosphor using ZnGa_2O_4 and $\text{CaO--Ga}_2\text{O}_3$ as host phosphors, the luminance of green and yellow emission of their devices are 230 cd/m², 261 cd/m², respectively, driven at 60 Hz. In order obtain a blue emission from oxide phosphors, Wang *et al.*¹⁰⁾ have prepared a composite oxide material, $\text{Gd}_3\text{Ga}_5\text{O}_{12}/\text{SiO}_2$, by combinatorial approach. Using this method, they have found some new luminescent materials.¹¹⁾

We prepared a blue-green EL emitting $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ TFEL by electron beam evaporation, and the thin film was annealed at 450°C for 3 h in air. The photoluminescence (PL), EL, and Photoluminescence excitation (PLE) spectra are investigated. In order to investigate the origin of emission peaks of PL and EL, the PL of the composite materials with different ratios of Gd_2O_3 to Ga_2O_3 without dopant are also investigated.

$\text{Gd}_3\text{Ga}_5\text{O}_{12}\text{:Ce}$ powder phosphor was prepared by mixing three components: Gd_2O_3 (purity 99.99%), Ga_2O_3 (99.99%) and Ce_2O_3 (99.99%). Their weights were chosen in order to get a stoichiometric compound of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ with Ce concentration at 1 at.%. The mixture of them was pressed into pellets, and then sintered at 1450°C for 3 h. The structure of devices is ITO/ Ta_2O_5 /phosphor/ Ta_2O_5 /Al. The insulator layer Ta_2O_5 was prepared by RF-sputter, the thickness of which is about 200 nm. The thin film $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ was prepared by electron beam evaporation with the thickness about 300 nm. In the process the substrate temperature

was kept at 200°C. The samples were annealed in air at 450°C for 3 h. The PL, EL, and PLE spectra were measured by means of SPEX fluorescence spectrophotometer. Optical absorption spectrum was measured with Shimadzu UV-31010PC UV-VIS-NIR Scanning Spectrophotometer.

The thin film phosphor for measuring X-ray diffraction (XRD) is deposited on a Si substrate with Rigaku Rint-2400 diffractometer using $\text{CuK}\alpha$ radiation. Figure 1 shows the diffraction patterns of as-deposited, annealed films and powder. The diffraction pattern of the powder phosphor is well correspondence with powder diffraction of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, which indicates that the component of the powder is a polycrystal of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and in a random orientation. From the broad band of as-deposited thin film we can know that the film without annealing is amorphous. When the thin film is annealed at 450°C for 3 h, the film have moderately preferred (400) orientation. However, there are some other diffraction peaks, the component of thin film should be indicated as multicomponent oxide: $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$.

The PL, PLE and optical absorption spectrum of $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$ thin film are shown in Fig. 2. The PLE peak lies at 328 nm when monitored at 390 nm. The PL emission peaks excited by 330 nm lie at 390 nm and a shoulder at 440 nm. From the absorption spectrum in Fig. 2, we can know that the excitation peak is well corresponding with the ab-

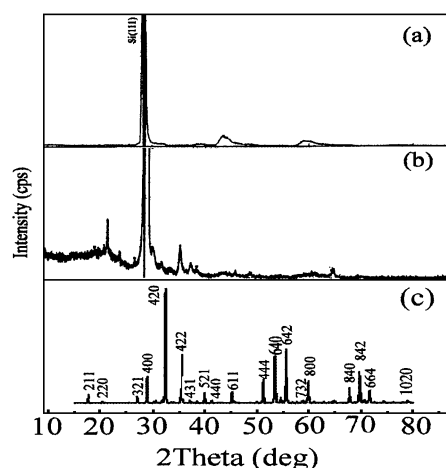


Fig. 1. XRD patterns of as-deposited(a), annealed (b) film, and powder (c) of $(\text{Gd}_2\text{O}_3\text{--Ga}_2\text{O}_3)\text{:Ce}$, the thickness of thin film is about 200 nm.

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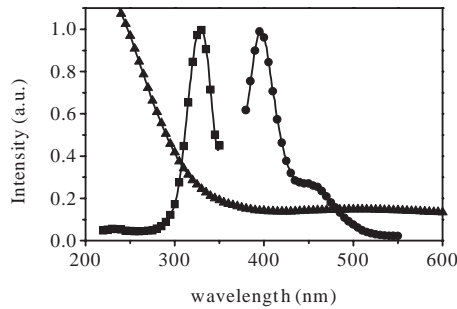


Fig. 2. The PL (●), PLE (■) and optical absorption (▲) spectra of $(\text{Gd}_2\text{O}_3\text{-Ga}_2\text{O}_3)\text{:Ce}$ thin film. The film for optical absorption measurement was deposited on the quartz substrate with the thickness about 15 nm.

sorption edge. However, We have not observed the emission from Ce^{3+} . In order to investigate the origin of the emission of the phosphor further, we prepared several powder samples with different ratios of Ga_2O_3 to Gd_2O_3 without dopant in the same condition as that for $(\text{Gd}_2\text{O}_3\text{-Ga}_2\text{O}_3)\text{:Ce}$. The ratios of Ga_2O_3 to $(\text{Ga}_2\text{O}_3+\text{Gd}_2\text{O}_3)$ are 100 at.%, 80%, 62.5%, 50%, 34.4%, 0%, respectively. The PL spectra of thin films corresponding to the powder samples are shown in Fig. 3 excited by 260 nm. From the figure, a PL emission at 435 nm was obtained from the powder of the pure Ga_2O_3 sintered at 1450°C. Because there are not any luminescent centers in pure Ga_2O_3 , we can obtain that the emission of 435 nm is original from the oxide vacancies of Ga_2O_3 due to high temperature sintering, which is like the green emission at 495 nm of ZnO phosphor.¹²⁾ With increasing the Gd_2O_3 from 37.5 at.% to 100 at.%, the PL emission is blue shift to 390 nm, and almost doesn't change any more. The emission of 390 nm can also ascribe to the oxide vacancy energy in the Gd_2O_3 . From all these above, we can conclude that the peaks at 390 nm and 430 nm are coming from the oxide vacancies.

The EL spectrum of the device is shown in Fig. 4, there are four peaks located at 358 nm, 390 nm, 440 nm, and 510 nm, respectively. The peaks of 390 nm and 440 nm are similar to the PL emission of the film. The emission at 510 nm is coming from transition from 4f-5d of Ce^{3+} .¹³⁾ For interpreting that 510 nm can only be seen in the EL, we give an interpretation as follows. The PLE of emission of 390 nm and 440 nm near the absorption edge, the excited electrons will prefer to the higher energy such as oxide vacancies and then combination in PL. In EL, however, the electrons are accelerated to excite the lower energy levels of Ce^{3+} early. Therefore, we can see the emission of Ce^{3+} in EL devices. The emission at 358 nm of EL is thought to come from shallow impurity energy level near the absorption edge, the real origin of this is not fully clear. The blue-green emission can be seen during the day in room when the EL device excited by a sinusoidal voltage with frequency at 1000 Hz. The threshold voltage of the devices is about 110 V.

In conclusion, we have fabricated a novel oxide TFEL device using $(\text{Gd}_2\text{O}_3\text{-Ga}_2\text{O}_3)\text{:Ce}$ as light emitting layer. The PLE of the thin film is well corresponding with the absorption edge of it. The PL emission at 390 nm and 440 nm are come from the oxide vacancy energy level of Gd_2O_3 and Ga_2O_3 , respectively. They are also found in EL of devices. Other two peaks are at 358 nm and 510 nm, the 358 nm is thought to come from the impurity energy levels near the absorption edge, the 510 nm is due to the 4f-5d transition of Ce^{3+} . The more work to obtain the higher blue emission will be investi-

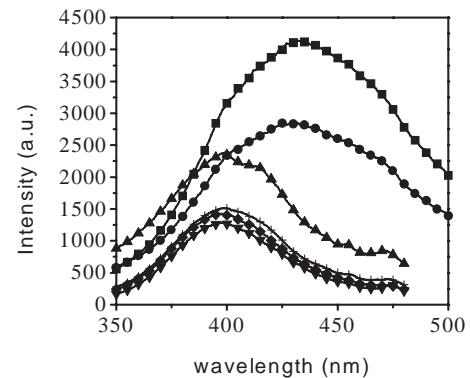


Fig. 3. PL of different composite materials excited by 260 nm. The ratio of $\text{Ga}_2\text{O}_3/(\text{Ga}_2\text{O}_3+\text{Gd}_2\text{O}_3)$ equals to 100 at.% (■), 80% (●), 62.5% (◆), 50% (▲), 34.4% (×), 0% (▼), respectively.

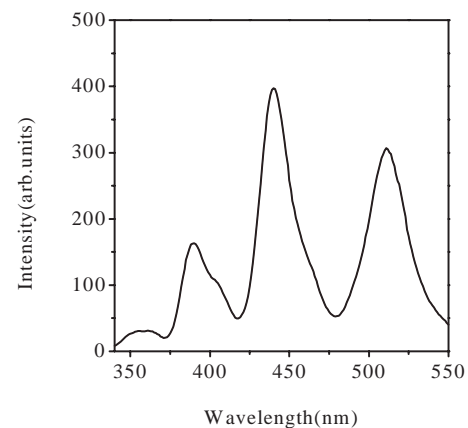


Fig. 4. EL of $(\text{Gd}_2\text{O}_3\text{-Ga}_2\text{O}_3)\text{:Ce}$ TFEL device.

gated recently.

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