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Manganese-activated gallium oxide EL phosphor thin films prepared using various deposition methods

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The luminescent properties of Ga_2O_3:Mn thin films prepared by magnetron sputtering or chemical methods such as solution coating and sol-gel techniques have been described. The electroluminescent characteristics were evaluated by thin-film electroluminescent (TFEL) devices using the Ga_2O_3:Mn thin films as the emitting layer. The photoluminescent and electroluminescent characteristics were mainly correlated to the crystallographical properties of the thin-film emitting layer. A luminance of 13.5 cd/m^2 was obtained in a TFEL device using an as-deposited Ga_2O_3:Mn thin film prepared by magnetron sputtering when driven at 1kHz. Luminances above 500 and 100 cd/m^2 were obtained in TFEL devices using annealed Ga_2O_3:Mn thin films regardless of the thin-film deposition techniques, when driven at 1 kHz and 60 Hz, respectively.

Keywords: Thin film, Electroluminescent device, Ga_2O_3:Mn, Oxide phosphor

1. Introduction

Gallium oxide (Ga_2O_3) has recently attracted widely interest as a new material for a gas sensor [1-4], transparent conductor [5,6] and phosphor [7]. Although the luminescent properties of â-Ga_2O_3 have been investigated [7,8], it has not been recognized as a phosphor until quite recently. Recently, â-Ga_2O_3 and amorphous Ga_2O_3 have attracted much attention as a new phosphor host material for thin-film electroluminescent (TFEL) devices.

High luminance multicolor emissions were obtained in TFEL devices composed of a Mn-activated Ga_2O_3 (Ga_2O_3:Mn) [9-11], a Ga_2O_3:Cr [12,13] or a Ga_2O_3:Eu [12,14-16] thin-film emitting layer and a thick ceramic insulating layer. However, the luminescent properties of Ga_2O_3 phosphor as well as the possibility of using it as the thin-film emitting layer for TFEL devices have yet to be clarified in detail.

In this paper, we describe the luminescent properties of â-Ga_2O_3:Mn thin films prepared on a thick ceramic sheet using various deposition methods.

2.Preparation of Ga_2O_3:Mn thin-film emitting layer

The Ga_2O_3:Mn thin films, thickness of 1-2 µm, were deposited by rf magnetron sputtering or chemical methods such as solution coating and sol-gel techniques. The Mn content (Mn/(Ga+Mn) atomic ratio) in Ga_2O_3:Mn thin films ranged from 0.1 to 5 atomic%. The photoluminescent (PL) and electroluminescent (EL) characteristics were measured using the Ga_2O_3:Mn thin films prepared on a $BaTiO_3$ thick ceramic sheet.

The PL characteristics were evaluated under a N_2-laser excitation or using spectrofluorophotometer (SHIMADZU RF-5300 PC). The EL characteristics were evaluated with a single-insulating layer-type TFEL device which the cross-sectional structure of the device is shown in Fig.1 [9-11,17]. Every constituent (back Al electrode thermally evaporated on after heat treatment) of the device was an oxide material; *i.e.*, the emitting layer, insulating layer and transparent electrode were composed of a Ga_2O_3:Mn phosphor thin film, thick $BaTiO_3$ ceramic sheet insulator (thickness of about 0.2 mm) and aluminum-doped zinc oxide (ZnO:Al) transparent conducting thin film, respectively. The EL characteristics of the TFEL devices driven by an ac sinusoidal-wave voltage were measured using a Sawyer-Tower circuit, an AC power meter and a conventional luminance meter.

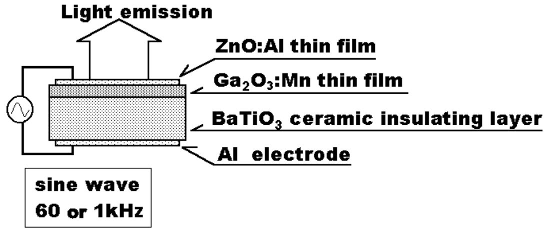

Fig.1 Cross-sectional structure of the TFEL device.

In rf magnetron sputtering, a mixture of Ga_2O_3 and MnO_2 powders calcined at 1000 °C in Ar was used as the target. The Ga_2O_3:Mn phosphor thin films were deposited under the following conditions: atmosphere, pure argon; pressure, 6 Pa; substrate temperature, 200-500 °C; target-substrate distance, 25 mm; and target, Ga_2O_3:Mn phosphor powder. In dip coating methods, we used two kinds of chemical solutions; a solution of source materials dissolved in methanol and sol-gel process.

In the former, gallium acetylacetonate ($Ga(C_5H_7O_2)_3$) and manganese chloride ($MnCl_2$) were used as the gallium and manganese sources, respectively. The $BaTiO_3$ ceramic sheets were immersed in a solution of source materials dissolved in methanol (CH_3OH). These solution coated ceramic sheets were subsequently heated in a furnace for 30 s at 600-950 °C. In the latter, trimethoxy gallium $Ga(OCH_3)_3$ and $MnCl_2$ were initially dissolved in CH_3OH by stirring at room temperature (RT) for 30 min in a N_2 gas atmosphere. Subsequently, H_2O and HCl were added and stirred at RT for 1 h under N_2 gas.

The ceramic sheet substrates were dipped in the solution, dried and then heat-treated at 300-900 °C. Here, we refer to these processes as the first step heat treatment in the following description. These processes were repeated from 15 to 30 times in order to obtain a thickness of 1-2 μm. In order to improve the luminescent properties, all deposited Ga_2O_3:Mn thin films were postannealed in an Ar gas atmosphere for 0.5-1 hour at about 1020 °C, regardless of the deposition techniques.

3. Results and discussion

A. Ga_2O_3:Mn thin films prepared by magnetron sputtering

The EL and PL characteristics in as-deposited Ga_2O_3:Mn thin films prepared by rf magnetron sputtering were strongly dependent on the deposition conditions such as the substrate temperature and sputter gas atmosphere. As-deposited Ga_2O_3:Mn thin films prepared at substrate temperatures up to about 350 °C were amorphous. When prepared above about 350 °C, however, the resulting thin films were crystallized and identified as β-Ga_2O_3. The green emission was also observed in PL under a N_2-laser excitation for crystallized Ga_2O_3:Mn thin films. As an example, typical luminance (L), transferred charge density (Q) and luminous efficiency (η) versus applied voltage (L-, Q- and η-V) characteristic data are shown in Fig.2 for TFEL devices using an as-deposited Ga_2O_3:Mn thin film prepared using the target with a Mn content of 1.0 at.% at a sputter gas pressure of 6 Pa with an oxygen partial pressure of 2%. A luminance of 13.5 cd/m^2 was obtained in the TFEL device with an as-deposited Ga_2O_3:Mn thin-film emitting layer prepared at a temperature of about 500 °C and driven at 1 kHz. In addition, the sputtered Ga_2O_3 phosphor thin films were postannealed in an Ar gas atmosphere for 1 hour at a temperature of 1020 °C. The amorphous Ga_2O_3:Mn thin films were crystallized by postannealing at a temperature above about 800 °C, as evidenced from X-ray diffraction analyses.

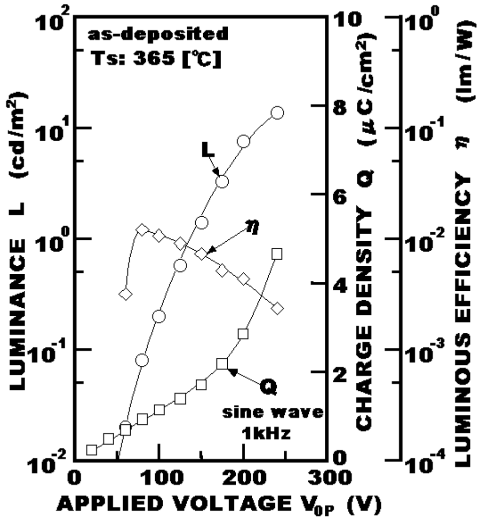

Fig.2 L-,Q- and η-V characteristics for TFEL device using an as-deposited Ga_2O_3:Mn thin film prepared by rf magnetron sputtering.

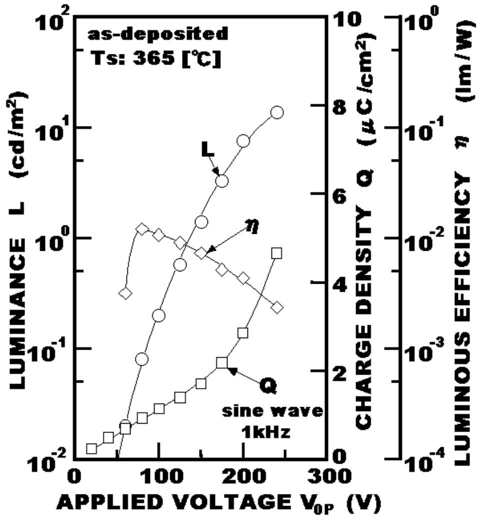

Fig.3 L-V characteristics for TFEL devices using annealed Ga_2O_3:Mn thin films prepared at various substrate temperatures by magnetron sputtering

The crystallinity of Ga_2O_3:Mn thin films improved considerably as the annealing temperature was increased up to about 1000 °C. The EL characteristics for TFEL devices using postannealed Ga_2O_3:Mn thin films were also dependent on the substrate temperature as well as the annealing temperature. Figure 3 shows the L-V characteristic as a function of the substrate temperature for TFEL devices using Ga_2O_3:Mn thin films prepared with a Mn content of 0.5 at.% and postannealed at 1020 °C in an Ar gas atmosphere. The obtained substrate temperature dependence of L-V characteristics was mainly related to the crystallinity of annealed Ga_2O_3:Mn thin-film emitting layers used in the TFEL devices.

B. Ga_2O_3:Mn thin films prepared by dip coating

The EL and PL characteristics in Ga_2O_3:Mn thin films prepared by dip coating methods were strongly dependent on the first heat treatment and annealing temperatures as well as the solution condition. Figure 4 shows a typical L-V characteristic as a function of the first heat treatment temperature for TFEL devices using Ga_2O_3:Mn thin films dip-coated from the solution of source materials dissolved in methanol with a Mn content of 0.3 at.%. Although dip-coated Ga_2O_3:Mn thin films were amorphous immediately after the first heat treatment up to 950 °C was carried out for 30 s, the thin films annealed at 1020 °C in an Ar gas atmosphere were β-Ga_2O_3. In PL under a N_2-laser excitation, the strong green emission was observed for the crystallized Ga_2O_3:Mn thin films. As can be seen in Fig.4, the L-V characteristic was also improved considerably as the first heat treatment temperature was increased up to about 800 °C. The first heat treatment temperature dependence of L-V characteristics was also related to the crystallinity of Ga_2O_3:Mn thin-film emitting layers.

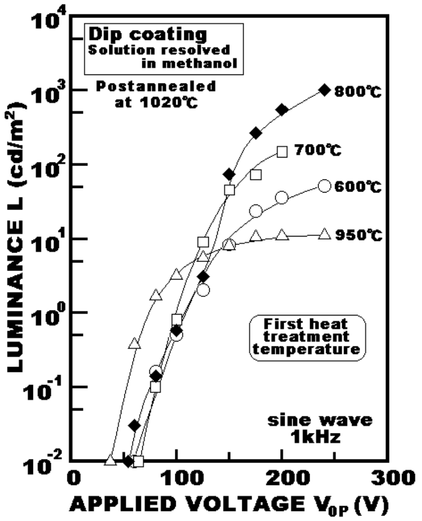

Fig.4 L-V characteristics for TFEL devices using annealing Ga_2O_3:Mn thin films prepared at various first heat treatment temperature by dip-coating with a solution.

In addition, the L-V characteristic of TFEL devices using Ga_2O_3:Mn thin films dip-coated with sol-gel process were strongly dependent on the first heat treatment temperature. Figure 5 shows a typical L-V characteristic as a function of the first heat treatment temperature for TFEL devices using annealed Ga_2O_3:Mn thin films dip-coated with a Mn content of 0.3 at.% by sol gel-process. The Ga_2O_3:Mn thin films annealed at 1020 °C in an Ar gas atmosphere were β-Ga_2O_3. The strong green emission was also observed on PL measurements under a N_2-laser excitation for crystallized Ga_2O_3:Mn thin films. As can be seen in Fig.5, the L-V characteristic was also improved considerably as the first heat treatment temperature was increased up to about 900°C.

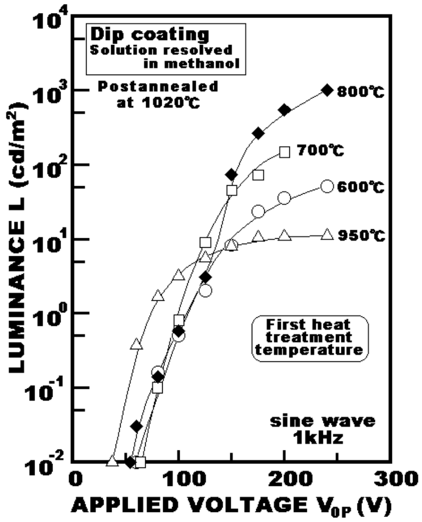

Fig.5 L-V characteristics for TFEL devices using annealed Ga_2O_3:Mn thin films prepared at various first heat treatment temperatures by dip-coating with a sol-gel process.

C. Comparison of EL characteristics

Figures 6, 7 and 8 show the comparison of obtained EL characteristics between TFEL devices using a sputtered Ga_2O_3:Mn thin film and dip-coated Ga_2O_3:Mn thin films prepared with the solution of source materials dissolved in methanol or sol-gel process, respectively. These TFEL devices were fabricated using Ga_2O_3:Mn thin films annealed at 1020 °C in an Ar gas atmosphere for 1 hour and prepared under the optimized preparation conditions as mentioned above. In addition, it was found that spectra of EL emission from these Ga_2O_3:Mn TFEL devices are equal to those of PL emission from the Ga_2O_3:Mn thin-film emitting layers used..

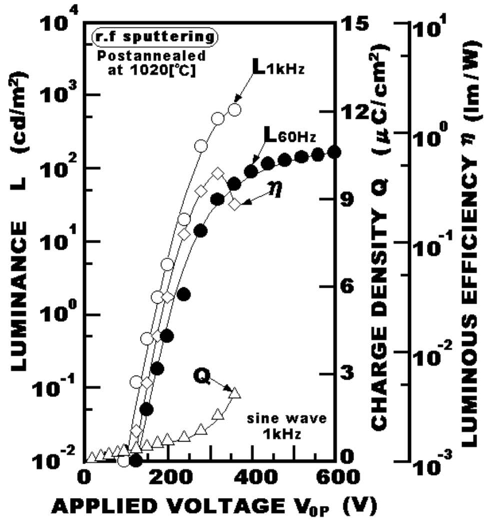

Fig.6 L-, Q- and η-V characteristics for a TFEL device using as annealed Ga_2O_3:Mn thin film prepared by rf magnetron sputtering, when driven at 1kHz (open) and 60Hz(solid),respectively.

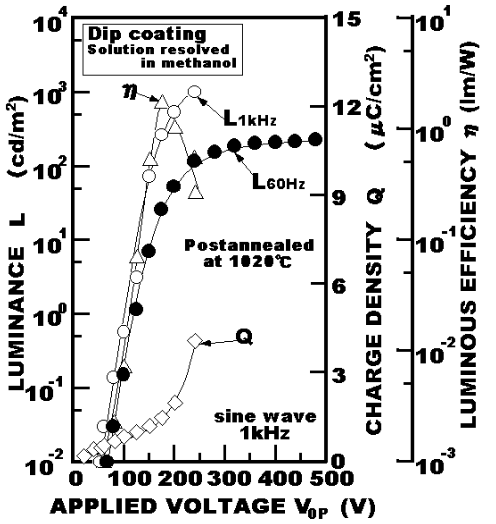

Fig.7 L-, Q- and η-V characteristics for a TFEL device using as annealed Ga_2O_3:Mn thin film prepared by dip coating with a solution, when driven at 1kHz (open) and 60Hz(solid),respectively.

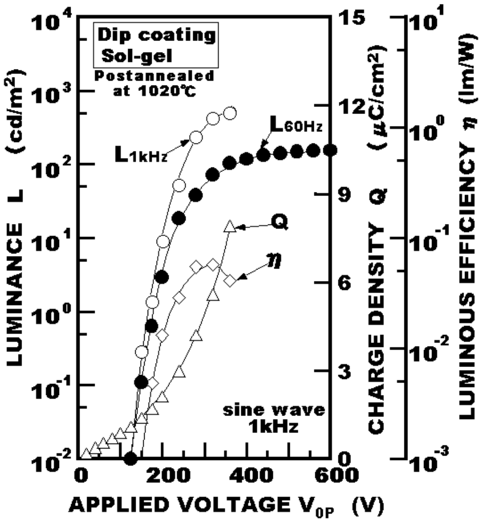

FIG.8 L-, Q- and η-V characteristics for a TFEL device using as annealed Ga_2O_3:Mn thin film prepared by dip coating with sol-gel process, when driven at 1kHz (open) and 60Hz(solid),respectively.

It should be noted that high luminances of 1018 and 227 cd/m^2 were obtained in a device using a dip-coated Ga_2O_3:Mn thin-film emitting layer and driven at 1 kHz and 60 Hz, respectively maximum luminous efficiency of 1.7 lm/W was obtained in the device driven at 1 kHz. In addition, high luminances of 627 and 167 cd/m^2 were obtained in a device using a sputtered Ga_2O_3:Mn thin-film emitting layer and driven at 1 kHz and 60 Hz, respectively. A maximum luminous efficiency of 0.42 lm/W was obtained in the device driven at 1 kHz. The difference of obtained luminances between dip-coated and sputtered Ga_2O_3:Mn TFEL devices was mainly related to the crystallinity and Mn content of the thin-film emitting layers.

4. Conclusions

The relationship between luminescent properties and crystallographical properties was investigated for as-deposited and annealed Ga_2O_3:Mn thin films prepared using various deposition techniques. The Ga_2O_3:Mn thin films were prepared by physical methods such as magnetron sputtering or chemical methods such as solution coating and sol-gel techniques. The crystallized Ga_2O_3:Mn thin-film emitting layers were always identified as β-Ga_2O_3. The PL and EL characteristics were mainly correlated to the crystallographical properties of the thin film emitting layers. A luminance of 13.6 cd/m^2 was obtained in a green emitting TFEL device using an as-deposited Ga_2O_3:Mn thin film prepared at temperatures of about 500°C by magnetron sputtering when driven at 1kHz. It should be noted that high luminances above 500 and 100 cd/m^2 for a green emission were obtained in the TFEL devices using annealed Ga_2O_3:Mn thin films regardless of the thin-film deposition techniques, when driven at 1 kHz and 60 Hz, respectively. Higher luminances were always obtained in TFEL devices using dip-coated Ga_2O_3:Mn thin films rather than sputtered films. The difference of obtained luminance was mainly related to the crystallinity and Mn content of the thin-film emitting layers.

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