Photoluminescence spectroscopy of highly oriented Y$_2$O$_3$:Tb crystalline whiskers

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Abstract

The crystalline state of terbium-containing yttria is one of the important candidates for uses to ultraviolet- and electron-excited green phosphors. To increase the intensity of green emission, structural design of the polycrystalline Y$_2$O$_3$:Tb was carried out using a chemical-vapor-deposition technique operated under atmospheric pressure. The green luminescence intensity was strongly dependent upon the concentration of Tb. The intensity of the photoluminescence at 542 nm obtained from $h_{100}$ oriented Y$_2$O$_3$:Tb whiskers was higher than that obtained from the uniform Y$_2$O$_3$:Tb polycrystalline film with random orientation.

Keywords: Y$_2$O$_3$:Tb; CVD; Orientation; Whisker; Phosphor; Polycrystal; Photoluminescence

1. Introduction

Photoluminescence of metal oxides has been widely investigated by numerous research groups. In particular, rare-earth-containing yttria (Y$_2$O$_3$:RE) is one of the most important metal oxides for luminescence study due to its advantages such as high luminescence efficiency, capability of doping for several rare-earths and ability of excitation by ultraviolet or electron irradiation. West et al. produced photoluminescent thin films of Y$_2$O$_3$:Eu by low-pressure metalorganic chemical-vapor-deposition (CVD). They measured the photoluminescent lifetimes of the films as a function of temperature using excimer laser excitation at 248 nm. Subsequent annealing at 1200°C in air enhances and stabilizes the luminescence [1]. In addition, Cho et al. demonstrated that the increase in brightness is attributed to the rough surface morphology which results in reduced internal reflections using high quality Y$_2$O$_3$:Eu phosphor films deposited on the diamond-coated silicon substrates [2]. Furthermore, Goldburt et al. found that the luminescent efficiency of the nanocrystalline Y$_2$O$_3$:Tb phosphors increased with the decrease in the particle size from 100 to 40 Å. This correlation was obtained from microstructural studies performed using transmission electron microscopy and luminescent measurements [3].

We have developed a CVD technique operated under atmospheric pressure for growth of amorphous and crystalline metal oxide films such as ZnO [4,5], ZnO:Al [6] and TiO$_2$ [7–10]. Our CVD setup is fundamentally a type of thermal CVD. However this setup possesses the abilities of design of microarchitecture of the metal oxide crystallites, epitaxy and non-epitaxy process with high growth rate, operation without vacuum system. For example, highly oriented ZnO epitaxial whiskers are the product of our CVD method [4,5]. In this study, random oriented Y$_2$O$_3$:Tb polycrystalline films and highly oriented Y$_2$O$_3$:Tb whiskers were synthesized using the CVD technique operated under atmospheric pressure. The analytical results for morphology, crystalline orientation and photoluminescence characteristics of the crystalline samples are described and discussed.

2. Experimental

The single crystalline wafer of (100) silicon substrate was cut into $10 \times 10 \times 0.5$ mm$^3$ and then washed with deionized water for 30 min. After the treatment, the single
To obtain the growth with preferential orientation, the Y$_2$O$_3$;Tb films were synthesized at the temperature region in which inhomogeneous gas reaction occurs. As the surface reaction was dominant, a few polycrystalline films demonstrated preferential orientation as shown in Fig. 2. All these samples formed on the silicon substrate had defective fluorite structure having relatively strong intensity at 29.2, 33.8, 48.5, 57.6 and 71.1° corresponding to (222), (400), (440), (622) and (800) diffraction lines. No diffraction lines indexed as the polycrystalline state of terbium oxide were observed. For the film grown at a vaporizing temperature of 180 °C, the intensity ratio of each diffraction line was nearly same as that of reference powder diffraction (ICDD Card No. 41–1105). The pattern obtained at a growth temperature of 210 °C was completely different from the powder pattern. The peak intensity of the (222) diffraction line decreased while the peak intensity of the (400) diffraction line increased, indicating preferential orientation of (100) crystalline direction of Y$_2$O$_3$;Tb. In addition, full width at half maximum for all diffraction lines of the sample grown at 210 °C was narrower than those of the sample deposited at 180 °C.
The degree of orientation estimated by the Lotgering orientation factor $f_{hkl}$ defined as

$$f_{hkl} = \frac{P_{hkl} - P_0}{(1 - P_0)},$$

where $P_{hkl}$ and $P_0$ are the peak intensity ratio of oriented direction to all directions of oriented sample, and that of powder of the standard specimen, respectively. Therefore, $f_{100}$ and $f_{111}$ were calculated using $P_{400}$ and $P_{222}$, respectively. The pattern obtained from the sample at a growth temperature of 210 °C showed $f_{100} = 0.85$, while that obtained from the sample with a growth temperature of 180 °C showed $f_{100} = 0.38$ indicating that the former one is preferentially oriented to $h_100i$ crystal-line direction.

Fig. 3 and 4 show a series of the SEM micrographs of the cross-section and the surface of the samples. The average grain size of the crystallites in the sample obtained at 180 °C is 5 μm. The growth orientation and shape of the crystallites are slightly random for each crystallite. However, the shape of the crystallite is uniform whisker. The size of the whisker of the sample obtained at 210 °C was determined as 1.5 μm and 5 μm in diameter and length, respectively. The size was confirmed by the top view and along to growth direction. The growth orientation is relatively aligned among whiskers.

Fig. 5(a) and (b) illustrates the photoluminescence spectra of the Y$_2$O$_3$:Tb films obtained at 180 and 210 °C, respectively. The peaks at 542 nm assigned to $^5D_4 \rightarrow ^7F_5$ transition as well as the most intense one at 484 nm assigned to $^5D_4 \rightarrow ^7F_6$ transition were seen on the spectrum.

These results suggest that the intensity is strongly dependent upon the concentration of Tb. Fig. 6 shows relative intensity of the luminescence at 542 nm for random oriented films and 〈100〉 oriented whiskers. The film thickness and the whisker length were kept constant at 5 μm. The intensity of the photoluminescence obtained from 〈100〉 oriented Y$_2$O$_3$:Tb whiskers was higher than that obtained from the uniform polycrystalline film with random...
orientation. Although the random oriented film possesses the maximum intensity at the Tb concentration of 2.0 at.%, the intensity keeps increasing to 1.5 at.% for the $\langle 100 \rangle$ oriented film. To our knowledge, the relationship between the green luminescence properties of $\text{Y}_2\text{O}_3$:Tb and Tb concentration has been still unknown. However, the optimum Eu concentrations in obtaining intense luminescence from the $\text{Y}_2\text{O}_3$:Eu whiskers is also different from that obtained at the uniform films [11].

The luminescence characteristic of the $\langle 100 \rangle$ oriented $\text{Y}_2\text{O}_3$ whisker with heavy dope of Tb may be different from that of the crystalline particle of $\text{Y}_2\text{O}_3$:Tb. First, the whiskers include more doping element into the lattice. For example, the ZnO whiskers have an Al solubility of more than 2 at.%, which is higher than that observed in the polycrystalline ZnO films [12]. Substitutional doping of Tb to the optimum lattice position is a possible reason to introduce intense luminescence. Second, microarchitecture of the aggregation of the $\text{Y}_2\text{O}_3$ crystallites may assist to increase photoluminescence. Although the total volume of the crystal of the aggregation of the whiskers is less than that of the uniform film, the surface area directly irradiated by the UV lamp on the whisker sample is larger than that of the film. Further investigation is required to clarify the luminescence mechanism of the whisker.

4. Conclusion

The random oriented $\text{Y}_2\text{O}_3$:Tb polycrystalline films and highly oriented $\text{Y}_2\text{O}_3$:Tb whiskers were synthesized using the CVD technique operated under atmospheric pressure. The photoluminescence intensity of $\text{Y}_2\text{O}_3$:Tb polycrystalline films and highly oriented $\text{Y}_2\text{O}_3$:Tb whiskers indicated that although random oriented film possesses the maximum intensity at the Tb concentration of 2.0 at.%, the intensity keeps increasing to 1.5 at.% for the $\langle 100 \rangle$ oriented whiskers.

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