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Dependence of photoluminescence of Bi-doped Y_2O_3 phosphor thin films on oxygen content in the sputtering atmosphere

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ABSTRACT

Photoluminescence (PL) emission properties of Bi-doped Y_2O_3 (Bi:Y_2O_3) phosphor thin films were investigated depending on the oxygen content in the sputtering atmosphere to find out the optimal oxygen content for obtaining Bi:Y_2O_3 phosphor thin film with strong PL emission intensity. PL emission intensity was greatly increased by adding a small amount of oxygen to the sputtering atmosphere. However, it was gradually decreased with further increasing the oxygen content. This behavior is thought to be due to the variation of crystallinity and surface roughness of the film depending on the oxygen content in the sputtering atmosphere. The film crystallinity showed similar behavior to PL emission intensity and the surface roughness except the case of Ar only was also decreased gradually with increasing the oxygen content. Density of point defects such as oxygen vacancy and interstitial in the film was expected to be changed according to the oxygen content in the sputtering atmosphere and also this change was considered to have an effect on the PL emission intensity of the Bi:Y_2O_3 film. In this work, Bi:Y_2O_3 phosphor thin film with the strongest PL emission intensity could be fabricated with the oxygen content of 10% in the sputtering atmosphere.

1. Introduction

One way to enhance the efficiency of solar cell is to minimize the optical energy losses of the solar energy such as a sub-band gap transmission loss and a lattice thermalization loss by using solar spectrum converter that can convert the solar spectrum to better match with absorbable energy range of the solar cell [1]. That is, either too high- or too low-energy of photons in the solar spectrum are converted into the suitable energy range for solar cells through down-conversion and up-conversion, respectively, using luminescent materials. It is known theoretically that the energy conversion efficiency of a single junction crystalline Si solar cell can be enhanced from 29% to 38.6% by solar spectrum converting [2,3].

Yttrium oxide (Y_2O_3) has many merits for phosphor host material such as low phonon energy (600 cm^{-1}), broad optical transparency (0.2–8 μm) due to large energy band gap (5.8 eV), high dielectric constant (14–18), high refractive index (2), and low absorption (from near-UV to IR) [4–6]. Bi^{3+} ions are commonly used to activate oxide materials, including phosphates, and borates [7–9]. Bi^{3+} ions have $6s^2$ electronic configuration, with the ground state corresponding to the $^1S_0$ and the first excited state to $^3P_0$, $^3P_1$, $^3P_2$, and $^1P_1$ for increasing excitation energies [10,11]. They show a broad and high absorption through the allowed $^1S_0 \rightarrow {}^3P_1$ transition in the range of 300–400 nm and a broad and strong emission in the visible region via $^3P_1 \rightarrow {}^1S_0$ transition when doped in Y_2O_3 host. So, Bi^{3+} ion doped Y_2O_3 (Bi:Y_2O_3) phosphor has been greatly investigated and also Bi:Y_2O_3 with co-doing lanthanide ions, in which Bi^{3+} ion plays a role as a sensitizer, has been reported [12–15]. These all can be used as a solar spectrum converter to enhance the efficiency of the solar cells.

Phosphor thin films, rather than phosphor powders, are suitable for solar spectrum converting to enhance the solar cell efficiency because phosphor powders give rise to adverse light scattering with energy loss [16]. However, they show weaker photoluminescence (PL) emission intensity than powders due to smaller interaction volume contributing to emission. Although increasing the film thickness, that is, increasing the interaction volume contributing to emission can be a solution to overcome this problem, however, there is a limit to the increment of the film thickness considering the film transmittance. Severe decrease in transmittance was observed in the Bi:Y_2O_3 phosphor thin film with a thickness of ~1.5 μm although the PL intensity increased gradually with increasing the film thickness as shown in our previous work [7]. To increase PL emission intensity, control of substrate temperature [13] or Bi concentration [7,14] have been investigated. Therefore, in this work, as a way to increase the PL emission intensity of the Bi:Y_2O_3

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phosphor thin film, we investigated the effect of the oxygen content in the sputtering atmosphere on the PL emission intensity and found that the oxygen content in the sputtering atmosphere was one of important factors to increase PL emission intensity of the Bi:Y_2O_3 film.

2. Experiments

Bi-doped Y_2O_3 phosphor thin films were deposited on Si(100) substrates by using RF magnetron sputtering to investigate their PL emission characteristics depending on the oxygen content in the sputtering atmosphere. The oxygen content was varied from 0% to 50% by 10% step, controlling the flow rate of Ar and O_2 gases under the fixed total gas flow rate of 10 sccm. In this work, sputtering system with off-axis geometry was used to minimize resputtering effect and damage due to high energetic particles and to easily control film compositions. Two sputtering targets, Y_2O_3 and $Y_{1.9}Bi_{0.1}O_3$, were sputtered simultaneously with the same rf power of 100 watts to deposit Bi:Y_2O_3 films, in which rf power applied to each target was determined based on the previous study, giving the optimal Bi^{3+} ion concentration in the films [7]. Si substrates were cleaned using general semiconductor cleaning procedure and native oxide was removed by buffered oxide etchant [17,18]. Before deposition, the chamber was evacuated down to $\sim 6.7 \times 10^{-4}$ Pa and then filled with Ar and O_2 gases at a controlled ratio. The sputtering pressure was maintained to be 0.67 Pa during deposition. The substrate temperature (T_s) was fixed to 500 °C. Two sets of the films with thickness levels of 300 and 500 nm were prepared.

After deposition, crystal structure and composition of the film were analyzed by X-ray diffraction (XRD) with θ-2θ scan mode using Cu Kα ($\lambda = 1.5406$ Å) and X-ray fluorescence (XRF) with continuous X-ray using Rh target, respectively. Surface morphology and film thickness were observed by field-emission scanning electron microscopy (FESEM, x80K magnifications). Oxygen content in the film was measured by electron probe microanalysis (EPMA) with wavelength dispersive spectrometer. Surface roughness was measured by atomic force microscopy (AFM). Spectrometer (SPEX 340E) with a He-Cd laser excitation source ($\lambda = 325$ nm) was used to collect PL spectra of the films. All PL measurements were done at room temperature.

3. Results and discussion

The XRD patterns of the ~300-nm Bi:Y_2O_3 thin films are shown in Fig. 1 as a function of oxygen content in the sputtering atmosphere. All the XRD peaks were indexed by using JCPDS card files No. 04-002-5312

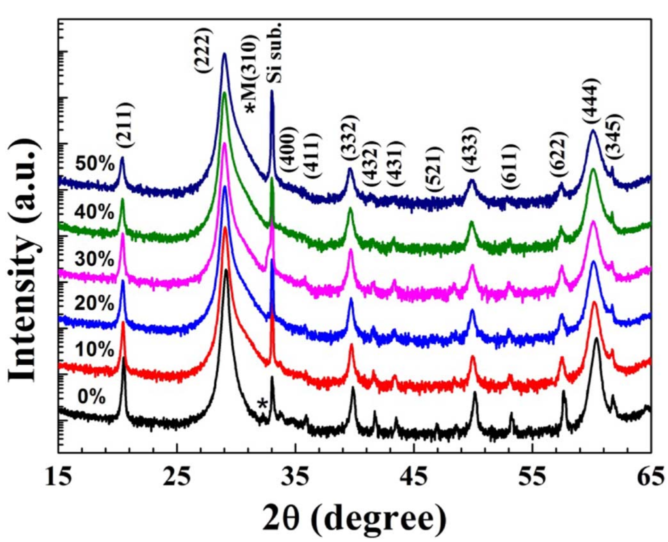

Fig. 1. XRD patterns of the Bi-doped Y_2O_3 thin films with a 300 nm thickness level depending on oxygen content in the sputtering atmosphere.

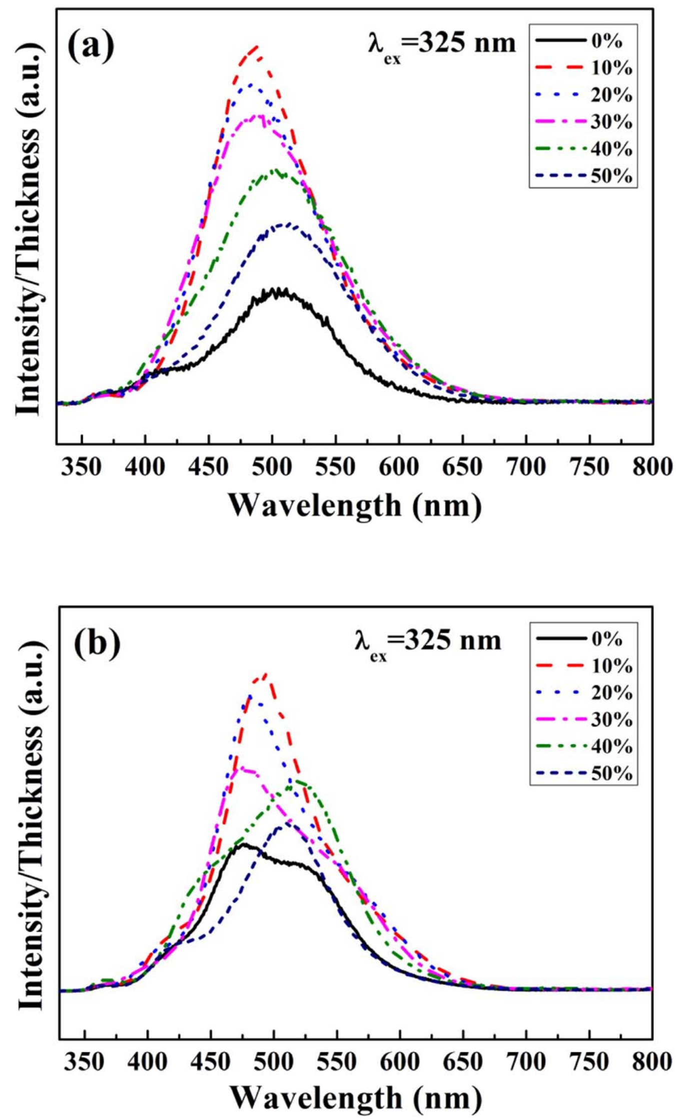

Fig. 2. Room temperature PL spectra of the Bi-doped Y_2O_3 thin films with (a) a 300 nm thickness level and (b) a 530 nm thickness level as a function of O_2 content in the sputtering atmosphere.

and 47-1274. As can be seen in Fig. 1, all the peaks could be indexed with a cubic structure except one weak peak related to monoclinic phase appeared in the XRD pattern of the film deposited without oxygen. This peak always appeared when the film was deposited in pure Ar and the peak intensity increased with increasing film thickness [7]. However, this monoclinic peak disappeared when only a small amount of oxygen, 10% in this work, was added to sputtering atmosphere, regardless of the film thickness. From these XRD results, it can be considered that formation of the monoclinic phase is attributed to the oxygen deficiency in the film. Consequently, pure cubic Bi:Y_2O_3 phosphor thin films with (222) preferred orientation could be fabricated by adding oxygen to the sputtering atmosphere.

Fig. 2 shows PL characteristics of the Bi:Y_2O_3 films with thicknesses of (a) 300 nm-level and (b) 500 nm-level depending on the oxygen content in the sputtering atmosphere. All the PL spectra in Fig. 2 were normalized by the film thickness to eliminate thickness factor affecting PL intensity [19]. As shown in Fig. 2(a) which is for 300 nm-level, the PL intensity was abruptly increased by adding only a small amount of oxygen (10%) to the sputtering atmosphere. However, the PL intensity was decreased gradually with further increasing oxygen content above 10%. This PL intensity dependence on the oxygen content in the