Applied Surface Science xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Annealing effect on properties of $BaWO_4:Eu^{3+}$ phosphor thin films grown on glass substrates by radio-frequency magnetron sputtering

Shinho Cho

Department of Materials Science and Engineering and Center for Green Fusion Technology, Silla University, Busan 46958, Republic of Korea

ARTICLE INFO

Article history:
Received 31 October 2016
Received in revised form 19 April 2017
Accepted 20 April 2017
Available online xxx

PACS Numbers:
78.20.-e
78.55.-m
81.20.Ev

Keywords:
Sputtering
Thin film
Rare earth
Photoluminescence

ABSTRACT

The effects of the rapid thermal annealing (RTA) temperature on the properties of $BaWO_4:Eu^{3+}$ phosphor thin films grown on glass substrates by radio-frequency magnetron sputtering were investigated. The deposited phosphor thin films were annealed at several RTA temperatures for 30 min. The experimental results show that the crystalline phase, surface morphology, transmittance, optical band gap, and photoluminescence intensity depended strongly on the RTA temperature. A preferential orientation along (112) plane and grains with an average size of 40 nm were observed for a thin film annealed at 400 °C. As the annealing temperature increased, the average transmittance in the wavelength range of 400–1100 nm gradually increased, reaching a maximum of 90.8% at 550 °C, where the highest optical band gap of 3.98 eV was obtained. The dominant emission spectra of the $BaWO_4:Eu^{3+}$ phosphor thin films under excitation at 323 nm, regardless of the RTA temperature, exhibited an emission band at 622 nm arising from the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions, indicating that the Eu^{3+} ions in the $BaWO_4$ host lattice were located at sites without inversion symmetry. The results suggest that the optimum annealing temperature for fabricating highly luminescent red-emitting phosphor thin films is 500 °C.

1. Introduction

Recently, there has been considerable interest in the fabrication of highly luminescent tungstate-based thin-film phosphors and the development of white light-emitting diodes (WLEDs) with a high color rendering index [1,2]. In particular, alkali earth metal tungstates are promising phosphor materials with potential applications in electroluminescent devices and optical fibers because of their high efficiency and good chemical stability. Of the two kinds of phosphors, thin-film phosphors have advantages over powder phosphors, including their good adhesion to solid surfaces, high resolution, superior luminescent properties, high degree of uniformity, and excellent thermal and mechanical stability [3]. These unique properties make thin-film phosphors promising candidates for developing high-quality electroluminescent devices and solid-state lighting. However, one important obstacle should be overcome before thin-film phosphors can be employed for new sources of white light for lighting and optoelctronic devices: the growth of highly luminescent thin-film phosphors. The low luminescent intensity of thin-film phosphors compared with that of powder phosphors depends on the inferior uniformity and crystallinity, high internal light trapping, and small interaction volumes under an excitation light source [4–6].

The development of the highly luminescent red-emitting phosphor thin films is important for their applications in WLEDs and solid-state lasers. Currently, most commercially available WLEDs are fabricated by coating yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ powder phosphors on a blue GaN LED chip (450–460 nm). These WLEDs have many restrictions in applications because of their low color reproducibility and poor color rendering index arising from the shortage of the red component [7]. Thus, the demand for novel red-emitting phosphor thin films with a crystalline grain size far smaller than that of powder phosphors has been rapidly increasing, and a clear understanding of the physical processes in thin films is necessary for developing reliable and reproducible materials and devices based on barium tungstates.

In this paper, we report the effects of the rapid thermal annealing (RTA) temperature on the structural, morphological, transmittance, optical band gap, and luminescent properties of Eu-doped $BaWO_4$ phosphor thin films grown on glass substrates by radio-frequency (rf) magnetron sputtering. The variations of the crystallinity and the emission intensity were examined with respect to the annealing temperature. Furthermore, we investigated the optimum annealing temperature for providing the highest luminescent intensity

E-mail address: scho@silla.ac.kr

http://dx.doi.org/10.1016/j.apsusc.2017.04.170
0169-4332/

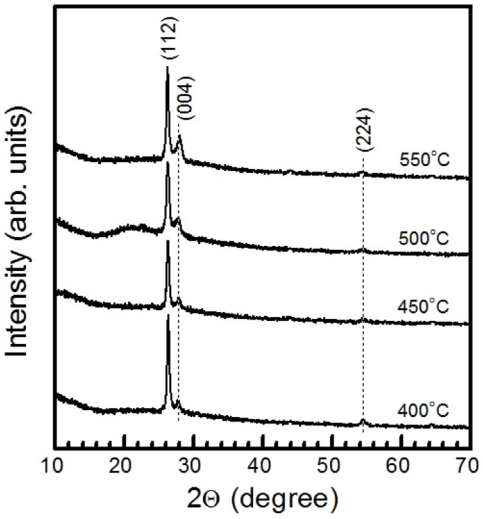

Fig. 1. XRD patterns of $BaWO_4$:Eu^{3+} phosphor thin films annealed at various RTA temperatures.

and the relationship between the annealing temperature and the optical band gap of the phosphor thin films.

2. Experiment

The $BaWO_4$:Eu^{3+} phosphor thin films were prepared on glass substrates by rf magnetron sputtering using a $BaWO_4$ ceramic target containing 5 mol% Eu_2O_3 (99.9% purity). After the deposition, thermal annealing was performed in a vacuum at temperatures of 400, 450, 500, and 550 °C for 30 min using a rapid thermal annealer. A 1-inch-diameter $BaWO_4$:Eu^{3+} target was synthesized using a conventional solid-state reaction method with $BaCO_3$ (99.98%), WO_3 (99.9%), and Eu_2O_3 as the raw materials. The mixed powders were calcined at 400 °C for 3 h, sintered at 1000 °C for 5 h in an electric furnace, and finally pressed using a hydraulic press into circular pellets with a diameter of 1 inch and a thickness of 15 mm. The sputtering chamber was initially evacuated to a vacuum on the order of 4×10^{-6} Torr, and then high-purity argon gas was introduced into the chamber through a mass flow controller. The working pressure was maintained at 30 mTorr, and the deposition was performed at 200 °C at an rf power of 40 W by rotating the substrate holder at a rate of 10 rpm.

The crystalline structure of the $BaWO_4$:Eu^{3+} phosphor thin films was investigated by X-ray diffraction (XRD, Ultima IV, Rigaku) using Cu-$K\alpha$ radiation ($\lambda = 0.15406$ nm). The surface and cross-sectional morphologies of the thin films were examined using a field-emission scanning electron microscopy (S-4800, Hitachi). The room-temperature photoluminescence (PL) spectra were characterized by a fluorescence spectrometer (FS-2, Scinco). The optical transmittance of the thin films was measured in the wavelength range of 200–1100 nm using an ultraviolet-visible-infrared spectrophotometer (Ultrospec-3300 pro, Amersham).

3. Results and discussion

Fig. 1 shows the XRD patterns of the $BaWO_4$:Eu^{3+} phosphor thin films annealed at RTA temperatures of 400, 450, 500, and 550 °C. The spectra of all four films exhibit a strong peak centered at 26.38° and two weak peaks at 27.82° and 54.64°. The former peak corresponds to the diffraction from the (112) plane of $BaWO_4$, and the latter two peaks are attributed to the (004) and (224) planes of $BaWO_4$, respectively. Preferential growth was observed along the (112) plane. All the diffraction peaks were indexed to the tetragonal structure of $BaWO_4$, as indicated in JCPDS #72-0746. The phases of the Eu^{3+} ions were not observed, indicating that the Eu^{3+} ions had no effect on the phase of $BaWO_4$. The dominant (112) diffraction peak for the $BaWO_4$:Eu^{3+} phosphor thin film annealed at an RTA temperature of 400 °C exhibited the highest intensity and the lowest full width at half maximum. As the RTA temperature was increased to 450 °C, the intensity of the main (112) peak reached its minimum, and then increased as the annealing temperature increased further, as shown in Fig. 1. The average grain sizes of the $BaWO_4$:Eu^{3+} phosphor thin films annealed at various RTA temperatures were calculated from the diffraction peaks along the main (112) plane using Scherrer's formula [8]. The $BaWO_4$:Eu^{3+} phosphor thin film annealed at 400 °C exhibited a grain size of approximately 25 nm.

Fig. 2 shows field-emission scanning electron microscopy (FE-SEM) images of the surfaces of the $BaWO_4$:Eu^{3+} films annealed at four different annealing temperatures. The surface morphology comprised numerous cobble-shaped crystalline grains with a size of nanometer and had no cracks or pores. Grains with an average size of 40 nm were observed for the phosphor thin film annealed at 400 °C, as shown in Fig. 2(a). As the annealing temperature increased, the grain size increased slightly, approaching its maximum at 450 °C, and then decreased gradually. The thin film annealed at 550 °C had a relatively narrow grain-size distribution.

Fig. 3 shows FE-SEM cross-sectional images of the $BaWO_4$:Eu^{3+} phosphor thin films annealed at several annealing temperatures. The phosphor thin films annealed at 400 and 450 °C had a columnar structure that was highly oriented, with the c-axis perpendicular to the substrate surface. The cohesion between the $BaWO_4$:Eu^{3+} thin film and the glass substrate was strong, and the surface of the thin film was smooth, as shown in Figs. Fig. 3(a) and (b). The thicknesses of all the samples were measured as 340 nm according to the lateral FE-SEM images. At annealing temperatures of 500 and 550 °C, the columnar patterns were tilted to the 1 o'clock position. The results are similar to those previously obtained for aluminum nitride thin films grown by rf reactive magnetron sputtering [9]. This phenomenon can be explained by the fact that the chemical interaction between WO_4^{2-} and Eu^{3+} ions is increasingly activated as the annealing temperature increases.

Fig. 4 shows the PL and excitation spectra of the $BaWO_4$:Eu^{3+} phosphor thin films annealed at several annealing temperatures. The excitation spectra of the $BaWO_4$:Eu^{3+} phosphor thin films monitored at 622 nm consist of a strong excitation band centered at 323 nm in the range of 300–360 nm, as shown in the inset of Fig. 4, which corresponds to the $^7F_0 \rightarrow {}^5D_4$ transition of Eu^{3+} ions [10]. The emission spectra were obtained by excitation at 323 nm and exhibit three typical emission bands at 597, 622, and 704 nm, which are attributed to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} ions, respectively [11]. As the annealing temperature increased from 400 to 500 °C, the intensity of the dominant red emission band at 622 nm gradually increased, approached its maximum at an annealing temperature of 500 °C, and then suddenly decreased at 550 °C because of the nonradiative energy transfer between Eu^{3+} ions. Among these three emissions, the most intense red band, which was centered at 622 nm, was ascribed to the $^5D_0 \rightarrow {}^7F_2$ forced electric dipole (ED) transition. On the other hand, the relatively weak emission bands at 597 and 704 nm corresponded to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole (MD) and $^5D_0 \rightarrow {}^7F_4$ ED transitions of Eu^{3+} ions, respectively [12]. Practically, the MD transition is not influenced by the chemical surroundings of the Eu^{3+} ions in the $BaWO_4$ host lattice, whereas the ED transition is highly sensitive to the local environment [13,14]. The relative intensity of the $^5D_0 \rightarrow {}^7F_2$ (622 nm) ED to $^5D_0 \rightarrow {}^7F_1$ (597 nm) MD transitions, which is called the asymmetry ratio, can be used to examine the local symmetry of the Eu^{3+} ions in the $BaWO_4$ host lattice. When Eu^{3+} ions in the host lattice are located at low-symmetry sites

Please cite this article in press as: S. Cho, Annealing effect on properties of $BaWO_4$:Eu^{3+} phosphor thin films grown on glass substrates by radio-frequency magnetron sputtering, Appl. Surf. Sci. (2017), http://dx.doi.org/10.1016/j.apsusc.2017.04.170