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Structural and luminescent properties of YAG:Ce thin film phosphor

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ABSTRACT

This work investigated the structural and luminescent properties of YAG:Ce (Ce-doped $Y_3Al_5O_{12}$) thin films grown at different deposition conditions. The YAG:Ce phosphor thin films were deposited on quartz at room temperature by rf magnetron sputtering. It was shown that the oxygen partial pressure in the sputtering gas and the rf power strongly affected the Al/Y atomic ratio, growth rate, crystallinity and luminescent properties of YAG:Ce films. The effect of the $O_2/(Ar + O_2)$ ratio on the composition prepared at RT differs from that prepared at high temperature. The growth rate of YAG:Ce films deposited at the gas ratio of $O_2/(Ar + O_2) = 0\%$ was significantly enhanced. Stoichiometric and polycrystalline YAG:Ce films were obtained in pure Ar. YAG:Ce films that were annealed in N_2 had a higher PL emission intensity than those annealed in air because annealing in N_2 prevents Ce^{3+} from the oxidation. We also found that transparency of YAG:Ce/quartz annealed at 1100 °C still was maintained, and YAG:Ce thin film has a transmittance of 75% including the substrate in the visible region. Annealing at temperatures above 1200 °C results in formation of SiO_2 crystalline phase. The sample annealed at 1200 °C has much lower transmittance but higher PL intensity than those of the sample annealed at 1100 °C.

1. Introduction

Ce-doped $Y_3Al_5O_{12}$ (YAG:Ce) has numerous applications such as a luminescent material in plasma display panels (PDPs) [1], solid-state lasers [2–4], and solid-state lighting [5–8], because of it has a high luminescent efficiency and chemical stability. Ce-doped YAG exhibits yellow emission from the characteristic 5d and 4f energy levels. The energy levels of the $5d^1$ excited states and the emission photon energy of Ce^{3+} ion strongly depend on the host crystals via the crystal field-induced energy level splitting of the $5d^1$ orbital [9,10]. Combined with a blue InGaN LED, Ce-doped YAG has been successfully used in white light emitting diodes (LEDs) [6–8].

The development of LEDs that emit blue or ultraviolet light has made the feasible production of LEDs that generate white light by the phosphor conversion from the LED to emission of a longer wavelength. The phosphor conversion is performed by incorporating a phosphor/epoxy hybrid with a reflector cup containing a LED chip [11,12]. The phosphor particles are randomly oriented and interspersed in the cured epoxy. One of the shortcomings for the phosphor/epoxy hybrid is that the uniform emission of white light from the LED is difficult to obtain. To overcome the weaknesses of using mixtures of phosphor powders and epoxies, thin-film phosphor has been used to convert primary light from LEDs in LED-phosphor lighting. In LED-phosphor lighting applications, phosphors of the thin film type support better methods of fabrication of white lighting systems and can be more conveniently integrated with LEDs and arrays of LEDs than those of the powder type can [10,13]. Few studies have examined the structure and luminescent properties of thin film YAG:Ce phosphors deposited at high substrate temperature (550 °C) [10,14]. However, the effect of compositional change of YAG:Ce phosphors deposited at RT on the photoluminescence has not been reported. According to Kim and Kim [14], YAG:Ce phosphor thin films were deposited at high substrate temperature (550 °C) by rf magnetron sputtering. Stoichiometric and polycrystalline YAG:Ce films can be obtained with 50% oxygen. However, introduction of gaseous oxygen in the sputtering dramatically reduces the sputtering rate of the film. Resputtering is accelerated by *in situ* heating of the substrate, which changes the Al/Y atomic ratio. A higher substrate temperature and a higher oxygen partial pressure lead to a lower growth rate of the films in the sputtering, a higher production cost, and detrimental effect in the scalability of the process. To improve the process proposed by Kim et al., the parameters of the sputtering of the YAG:Ce phosphor thin films must be optimized.

In this study, YAG:Ce phosphor thin films were prepared at room temperature by rf magnetron sputtering, and the effects of the sputtering parameters and the annealing conditions on the structural

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and luminescent properties of YAG:Ce phosphor thin films were studied.

2. Experimental

The YAG:Ce phosphor thin films were deposited from a 3 in. YAG:Ce ceramic target on quartz glass substrates by radio-frequency (rf) magnetron sputtering. The Al/Y atomic ratio in the YAG:Ce ceramic target was 1.48, which was slightly lower than the stoichiometric value of 1.67. The base pressure of the deposition chamber was 1×10^{-6} Torr and the working pressure during the film deposition was 5 mTorr. The substrate temperature was held constant at room temperature during the growth of the film. The target-to-substrate distance was 5 cm. Following deposition, the phosphor thin films were annealed at various temperatures in atmospheres of N_2 and air for 10 h to improve their crystallinity.

Film thickness was measured using a Profiler (Alpha step 500, Tencor, USA) with a diamond stylus, which was mechanically coupled to the core of a linear variable differential transformer. The transmittance spectrum was measured by a Shimadzu UV-160A spectrometer. The surface morphologies and compositions of the films were characterized using a scanning electron microscope (SEM, JEOL JSM 6480LV) and an energy dispersive X-ray spectrometer (EDS, Oxford INCA 350). The crystalline phases of thin films were identified using an X-ray diffractometer (XRD, Bede D1) with Cu K_α radiation ($\lambda = 0.15418$ nm) at a scanning speed of 4°/min. The chemical state of Ce in the annealed YAG:Ce thin film was examined by X-ray photoelectron spectroscopy (XPS, VG, ESCALAB 250) with a binding energy resolution of ~0.3 eV. Photoluminescence (PL) measurements were made using a PL spectrometer (Fluorolog-3-21, Jobin Yvon) with an excitation at 450 nm.

3. Results and discussion

Fig. 1 displays the Al/Y atomic ratios in the YAG:Ce phosphor thin films deposited at rf powers with gas ratios of $O_2/(Ar + O_2) = 0\%$ and 50%. Because a higher substrate temperature was associated with a lower growth rate of the films in the sputtering, the substrate temperature of all the films was kept constant at room temperature. The Al/Y atomic ratio deviated greatly from the target ratio at an rf power of 200 W. The ratio decreased as the rf power increased, approaching the stoichiometric composition at 300 W, revealing that the sputtering rate of Y and Al varied with the rf power [15]. Notably, the Al/Y atomic ratios at oxygen partial pressure of 0% were lower than those at 50%. The variation in the Al/Y ratio with the rf power is related to the change of Al and Y sputtering rate with an increase in the incident ion energy. However, when an oxide target is used and oxygen gas is introduced into in the sputtering gas, the reduction of the sputtering rate [16] or the resputtering probably affects the composition of the deposited film [17,18]. Resputtering was observed in YAG:Ce and the $ZnGa_2O_4$:Mn system. The addition of the oxidant to sputtering gas can influence the atomic ratio of the films due to the resputtering effect, which is exacerbated by *in situ* heating of the substrate [14,19]. In the experiments, the substrate temperature was kept constant at room temperature, and the effect of the $O_2/(Ar + O_2)$ ratio on the composition differs from that at high temperature. Thin films of aluminum oxide, yttrium oxide, and mixed oxides with the Y_2O_3/Al_2O_3 ratio were prepared by radio-frequency magnetron sputtering. Their variations in the sputtering rates have also been investigated at various deposition temperatures [20]. The sputtering rate decreased as the deposition temperature increased. The sputtering rate of Y_2O_3 deposited at room temperature was close to that of Al_2O_3, which result is similar to that herein. No resputtering effect at room temperature was found in that work. Therefore, the decrease in sputtering rate was more likely to be important to the change in the atomic ratio in the films herein. This fact may explain the compositional variation of the deposited films with oxygen partial pressure in the sputtering gas.

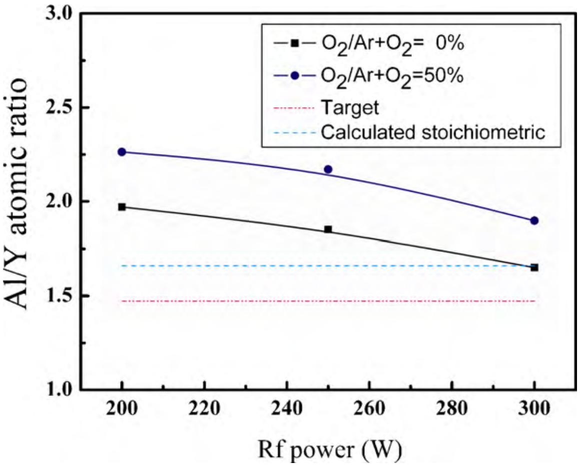

Fig. 1. Al/Y atomic ratio in YAG:Ce thin film phosphors deposited at rf powers with gas ratios of $O_2/(Ar + O_2) = 0\%$ and 50%.

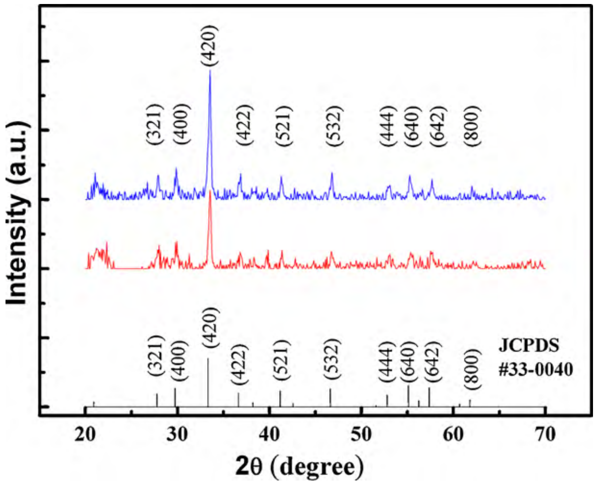

Fig. 2. XRD patterns of YAG:Ce films deposited at the gas ratios of $O_2/(Ar + O_2) = 0\%$ and 50% at rf power of 300 W, following annealing at 1100 °C for 10 h in an atmosphere of N_2. The vertical lines correspond to the JCPDS (#33-0040) indexing.

Fig. 2 presents X-ray diffraction (XRD) patterns of YAG:Ce films that were deposited at an rf power of 300 W in sputtering gas with the gas ratios of $O_2/(Ar + O_2) = 0\%$ and 50%. The films were annealed at 1100 °C for 10 h in N_2. The positions of the diffraction peaks match those in the standard pattern of the $Y_3Al_5O_{12}$ (YAG) phase, obtained by the Joint Committee on Powder Diffraction Standards (JCPDS-33-0040). Compared with the XRD patterns obtained at the different $O_2/(Ar + O_2)$ sputtering gas ratios, the result indicates that the crystallization of YAG:Ce films was poorer when the partial pressure of oxygen was higher.

This study also examined how the oxygen content in the sputtering gas affects the luminescent properties of films that were deposited at an rf power of 300 W and subsequently annealed at 1100 °C for 10 h in N_2 atmosphere. Fig. 3 displays the excitation and emission PL spectra of YAG:Ce phosphor thin films that were deposited at different $O_2/(Ar + O_2)$ ratios. The annealed films displayed an emission peak, whereas the as-deposited films gave none. The PL emission spectrum had a broad emission band that centered at 545 nm. This emission corresponds to the transition from the 5d excited state to the 4f ground state of the Ce^{3+} ion in the YAG crystal. The PL excitation spectrum includes two peaks at 340 nm (weak) and 450 nm (strong), which correspond to characteristic 5d and 4f energy levels. With reducing the oxygen partial pressure in the sputtering gas, the emission intensity increases due to improving the crystallinity. According to the result of PL spectra, the annealed thin films which were deposited at RT (without substrate heating) also had an emission peak. So to increase growth rate, the substrate temperature of all the films was kept constant at room temperature. Moreover, YAG:Ce phosphor thin films that

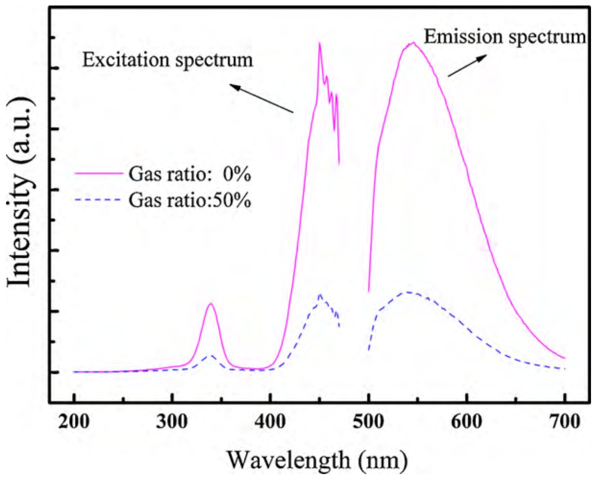

Fig. 3. Excitation and emission spectra of YAG:Ce deposited at the gas ratios of $O_2/(Ar+O_2)=0\%$, and 50%.

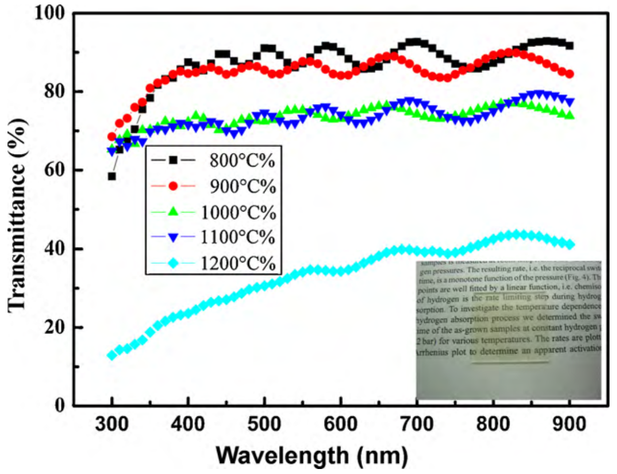

Fig. 5. Transmittance spectra of YAG:Ce films that were annealed at temperatures from 800 to 1200 °C for 10 h in an atmosphere of N_2. The inset shows photograph of YAG:Ce films annealed at 1100 °C for 10 h in an atmosphere of N_2.

were deposited at the gas ratios of $O_2/(Ar+O_2)=0\%$ and 50% had different growth rates. The growth rates of the thin films obtained at the gas ratios of $O_2/(Ar+O_2)=0\%$ and 50% at an rf power of 300 W had growth rates of 0.75 μm/h and 0.3 μm/h, respectively. Hence, oxygen changed growth rate of the YAG:Ce thin films to an extent that depended on its partial pressure. Figs. 1 and 2 demonstrate that well-developed polycrystalline YAG:Ce films grew at a rate of 0.75 μm/h, at the gas ratio of $O_2/(Ar+O_2)=0\%$ and an rf power of 300 W. This growth rate was twice higher than that obtained at the gas ratio of $O_2/(Ar+O_2)=50\%$.

Fig. 4 depicts XRD patterns of YAG:Ce films that were annealed at temperatures from 800 to 1200 °C for 10 h in N_2. The crystallinity of the film was poor when it was annealed at 800 °C, and became better when it was annealed above 900 °C. Well-developed polycrystalline YAG:Ce films were obtained by annealing them above 1000 °C. YAG:Ce films were measured by UV–vis spectroscopy. Fig. 5 shows the transmittance spectra of YAG:Ce films that were annealed at various temperatures for 10 h in an atmosphere of N_2. The transmittance declined as the annealing temperature increased due to increasing crystallinity of the sample, as presented in Fig. 4. The photograph of YAG:Ce films that were annealed at 1100 °C for 10 h in an N_2 atmosphere was also shown in the inset of Fig. 5. Since YAG:Ce is transparent and glass substrate is quartz, the words on the paper below the YAG:Ce/quartz can be clearly seen. The transmittance of the YAG:Ce films, including the substrate, is an average of around 75% (maximum: 78%, minimum: 70%) in the visible region (wavelengths of 400–800 nm).

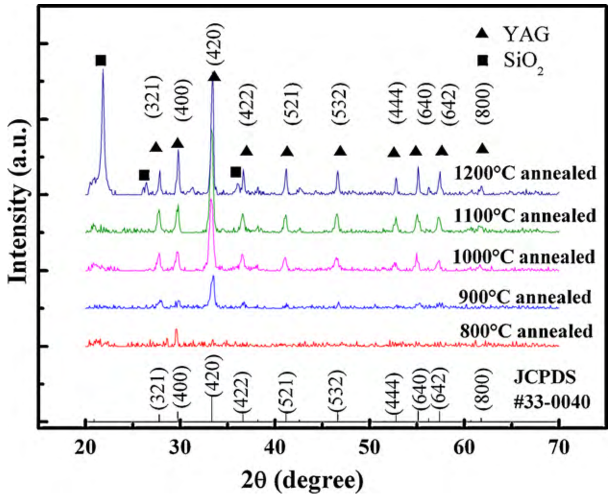

Fig. 4. XRD patterns of YAG:Ce films that were annealed at temperatures from 800 to 1200 °C for 10 h in an atmosphere of N_2. The vertical lines correspond to the JCPDS (#33-0040) indexing. (▲) YAG ($Y_3Al_5O_{12}$) and (■) SiO_2.

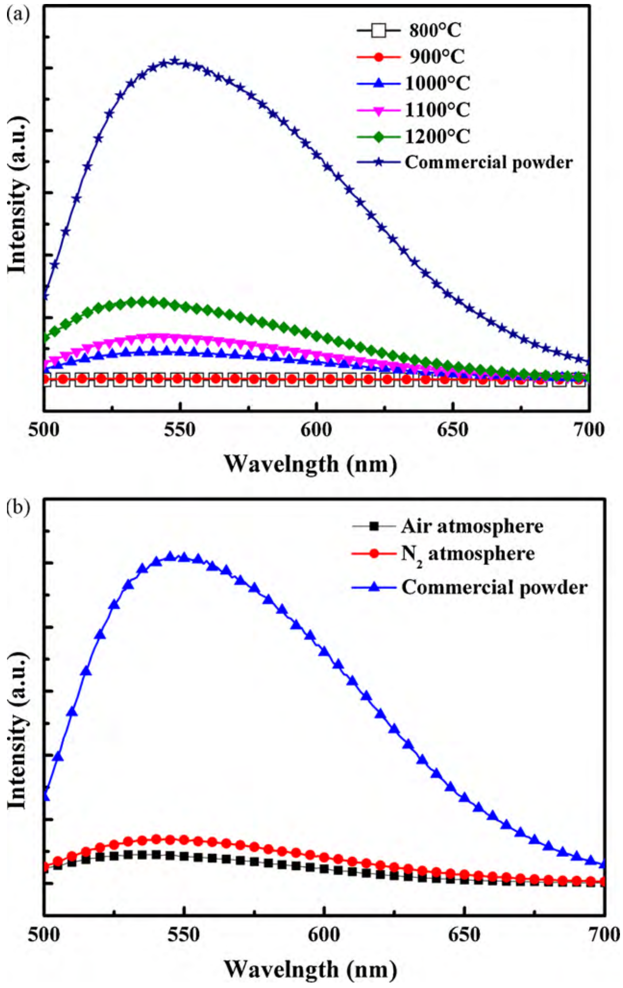

Fig. 6. (a) PL spectra of YAG:Ce films that were annealed at temperatures from 800 to 1200 °C for 10 h in an atmosphere of N_2. (b) PL spectra of YAG:Ce thin films that were annealed in air and N_2 atmosphere.

Fig. 6(a) displays the PL spectra of YAG:Ce films that were annealed at various temperatures for 10 h in an atmosphere of N_2. The intensity of the emission peak from the film that was annealed at 800 °C was very weak. The peak intensity increased with the annealing temperature because of the corresponding increase in YAG crystallinity. As revealed by in Fig. 4, annealing at temperatures above 1200 °C results in the formation of SiO_2 crystalline phase. In addition, the PL intensity of the commercial powder was 4.5 times higher than those of the film post-treated at 1200 °C. The film post-treated at 1200 °C had higher photoluminescence intensity than that post-treated at 1100 °C. So the optimum post-treatment temperature of the YAG:Ce phosphor film for application to white LED is 1200 °C because of high photoluminescence intensity. Furthermore, the energy conversion efficiency of silicon solar cell in yellow region is higher than that in blue region [21]. Solar cells increased the energy conversion efficiency by the phosphor conversion from the blue region to emission of a longer wavelength. The phosphor film post-treated at 1100 °C potentially could be used as luminescence conversion materials for application to solar cells due to their good transparency.

To examine how the annealing atmosphere affects the luminescent properties of YAG:Ce thin films, the as-deposited films were annealed in atmospheres of air and N_2. As shown in the Fig. 6(b), the PL intensity of the commercial powder was 8 times stronger than that of the as-synthesized phosphor film post-treated in N_2 atmosphere. YAG:Ce films that were annealed in N_2 had a higher PL emission intensity than those annealed in an atmosphere of air. The phosphor film post-treated in N_2 atmosphere had low PL intensity even though that film had high transparency. The result shows that the emission efficiency of a phosphor thin film is still considerably weaker than that of the powder phosphor.

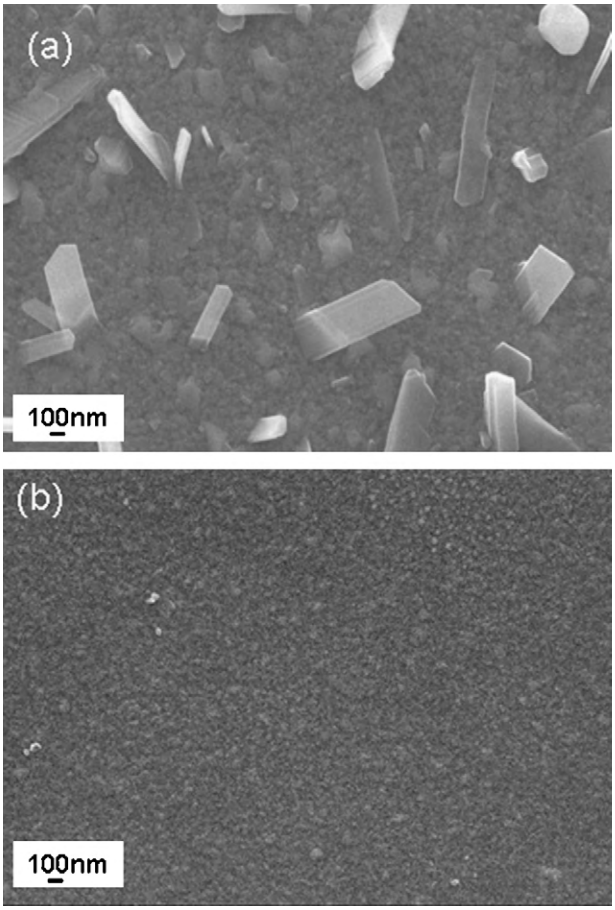

Fig. 7. SEM photographs of YAG:Ce thin films that were annealed in air (a) and N_2 (b).

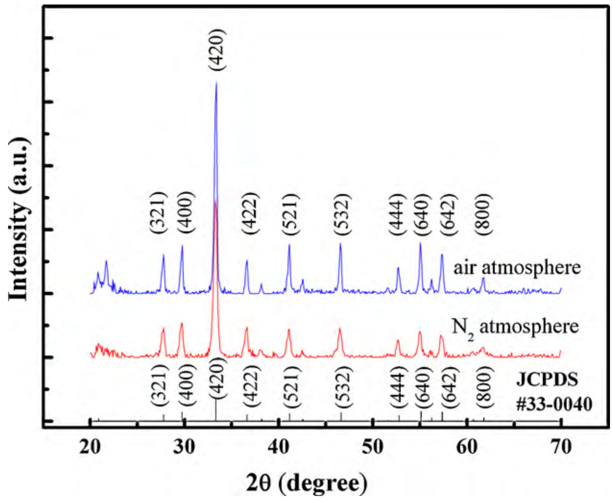

Fig. 8. XRD patterns of YAG:Ce thin films that were annealed in air and N_2. The vertical lines correspond to the JCPDS (#33-0040) indexing.

Figs. 7 and 8 present SEM photographs and XRD patterns of YAG:Ce thin films annealed in atmospheres of air and N_2, respectively. The film annealed in air had a rough surface and larger grains, while film annealed in N_2 was dense and had a smooth morphology, as displayed in Fig. 7. The XRD patterns also show that the films that were annealed in air had a higher crystallinity. The reason for the greater crystallinity of the films annealed in air is unclear, but it may be that the total oxygen content of the as-deposited film is less than the stoichiometric value, and annealing in air provides sufficient oxygen to form the crystalline phase of YAG.

Films with a higher crystallinity are theoretically expected to yield higher emission intensity. However, Fig. 6(b) shows contradictory results. In fact, the emission intensity also depends on the concentration of the activator, which was Ce^{3+} in this case. Su et al. [22] and Veith et al. [23] stated that the poor emission efficiency is caused by the redox reaction of cerium and the presence of defect centers. They suggested that the luminescence of YAG:Ce requires the cerium ions to be in trivalent states. In this work, the spectral features that are characteristic of either Ce^{3+} or Ce^{4+} species are used to identify the chemical state of cerium in the samples and the content of Ce^{3+}, Ce^{4+} were obtained. The estimated Ce^{3+}/Ce^{4+} atomic ratio was obtained from dividing the peak areas of Ce^{3+}

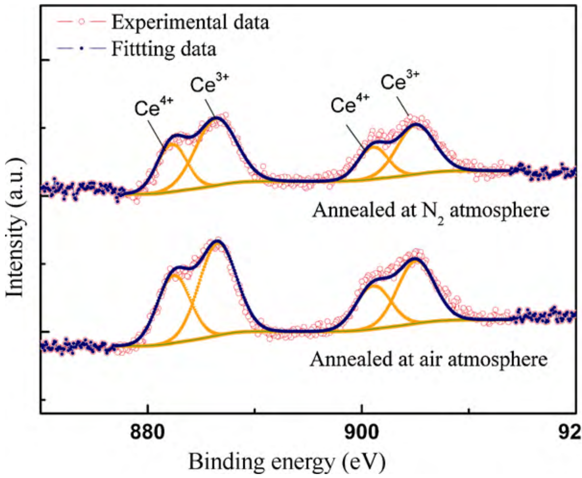

Fig. 9. XPS spectra of Ce 3d electron in YAG:Ce thin films that were annealed in air and N_2. Opened and closed circles plot experimental and fitted results, respectively.

$3d_{5/2}$ and Ce^{3+} $3d_{3/2}$ by those of Ce^{4+} $3d_{5/2}$ and Ce^{4+} $3d_{3/2}$. Fig. 9 presents the Ce 3d XPS spectra of the YAG:Ce thin films annealed in air and N_2. The Ce 3d XPS spectrum of the YAG:Ce thin films has four peaks (Ce^{4+} $3d_{5/2}$ at 882.26; Ce^{3+} $3d_{5/2}$ at 886.39; Ce^{4+} $3d_{3/2}$ at 901.04; Ce^{3+} $3d_{3/2}$ at 905.05 eV) [24]. The Ce^{3+}/Ce^{4+} atomic ratio in the thin films that had been annealed in air and N_2 were estimated to be 1.54 and 1.92. The concentration of Ce^{3+} activator in films that were annealed in N_2 significantly exceeded that of those annealed in air. The purging of N_2 during the annealing process can protect Ce^{3+} ions from oxidization, which is more likely to occur upon annealing in air. This fact explains why the film that was annealed in air with a high crystallinity had a lower emission intensity.

4. Conclusions

YAG:Ce yellow phosphor thin films were synthesized at room temperature by rf magnetron sputtering. The effects of rf power, sputtering gas and annealing conditions on the structural and luminescent properties of YAG:Ce films were studied. The changes of the Al/Y atomic ratio and the crystallinity of YAG:Ce films were caused by the rf power and the partial pressure of oxygen in the sputtering gas. When the substrate temperature was kept constant at room temperature, well-crystallized films were obtained at the gas ratio of $O_2/(Ar + O_2) = 0\%$, and the growth rate of the YAG:Ce films that were deposited at the gas ratio of $O_2/(Ar + O_2) = 0\%$ was 2.5 times higher than those deposited at the gas ratio of $O_2/(Ar + O_2) = 50\%$. Thin films that were annealed in N_2 had a higher PL emission intensity than those in air because more Ce^{3+} ions formed by the oxidation to Ce^{4+} ions were preserved. In addition, YAG:Ce thin film annealed at 1100 °C still exhibits good transparency in the visible region. The sample annealed at 1200 °C has much lower transmittance and higher PL intensity than those of the sample annealed at 1100 °C due to the formation of SiO_2 crystalline phase.

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