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Conversion of $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ to $Y_2Si_2O_7:Tb^{3+}$ thin film by annealing at higher temperatures

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ABSTRACT

$Y_3(Al,Ga)_5O_{12}$:Tb thin films were grown on Si(1 0 0) substrates in an Ar working atmosphere by using the pulsed laser deposition (PLD) technique. The $Y_3(Al,Ga)_5O_{12}$:Tb target was ablation deposited onto a Si(1 0 0) substrate using a 266 nm Nd:YAG laser. The influence of post deposition annealing temperature (1073 K to 1473 K) on the excitation and the emission bands, and the crystal structure of the thin film were monitored. X-ray diffraction (XRD) and photoelectron spectroscopy (XPS) depth profiles of the thin films indicate that there were annealing induced changes in the crystal structure and chemical composition causing changes in the excitation bands. These changes (structure and composition) are attributed to interdiffusion of atomic species between the substrate and the $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ thin film. The XRD and XPS data confirm that after annealing, $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ was converted to $Y_2Si_2O_7:Tb^{3+}$. A change in the relative ratios of the excitation band intensities was measured. Atomic force microscopy (AFM) showed that topographical changes also occurred during the annealing process. Thermoluminescence (TL) glow curves of the $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ thin films before and after annealing, indicated the presence of different types of traps resulting from the change on the structure of the thin films.

1. Introduction

Physics and technology of thin phosphor films play an important role in fabrication of smaller devices with high speed especially in the new generations of flat panel displays such as electroluminescent (EL) and field emission displays (FEDs). It is well documented that thin phosphor films have more significant advantages compared to the conventional powder such as high thermal stability, structural density, better adhesion to the underlying substrates and efficient dissipation of heat for high power operation [1]. Pulsed laser deposition (PLD) is a widely used technique to prepare thin phosphor films [2,3]. Amongst the luminescent materials, yttrium aluminum garnet ($Y_3Al_5O_{12}$) or YAG shows great luminescent properties when doped with rare-earth elements [4,5]. As reported in the literature [6–8], the brightness and the saturation characteristics of YAG were improved by the replacement of a portion of the Al with Ga in the matrix. $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ phosphor shows very good cathodoluminescent (CL) stability during prolonged electron bombardment [7] indicating that it is a promising phosphor candidate for FEDs and other applications. It should be noted that the aging of $Y_3Al_5O_{12}:Tb^{3+}$ in the epitaxial thin film form is much slower than in the powder form and this is probably due to better dissipation of heat in the epitaxial films [9]. It has been reported that in the initial period of electron irradiation $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ showed slow build-up of the luminescence intensity [9]. This phenomenon might be caused by a process in which the traps are slowly filled against thermal emptying. It was also found that the luminescence intensity could be increased instantaneously by co-doping with Yb^{3+} or Eu^{3+}. In addition, Yb^{3+} or Eu^{3+} are capable of decreasing the aging rate of $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ and $Y_3Al_5O_{12}:Tb^{3+}$. It is most likely that Yb^{3+} and Eu^{3+} prevent the feeding of traps responsible for the slow build-up or aging. It would therefore be interesting to monitor the effects of impurities on the luminescent properties of the thin films of either $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ or $Y_3Al_5O_{12}:Tb^{3+}$ phosphor. In this study, $Y_3(Al,Ga)_5O_{12}$:Tb thin films were pulsed laser deposited on Si(1 0 0) substrates in an Ar working atmosphere while the substrate temperature and other processing conditions such as the repetition rate, distance between target to substrate and laser energy density were kept constant during ablation. Post deposition annealing of the samples were found to cause diffusion of Si atoms from the substrate into the thin films. The mechanism of Si diffusion in the formation of silicates reported by Chiam et al. [10] is still not very clear. Generally, due to the need to break the covalent bonds, silicon mixing in oxides is not expected until a high temperature of 973 K is reached. However, some studies have shown that this mixing could occur at temperatures as low as 873 K when silicates are formed during the interdiffusion process. This temperature appears to be even lower at 573 K for the

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mixing of Y and SiO_2. As reported by Shin et al. [11], the formation of single-phase europium silicate crystals from EuO and SiO_2 requires temperatures as high as 2073 K for Eu_2SiO_4 and 1673 K for $EuSiO_4$. We could not find reports in the literature about the conversion of $Y_3(Al,Ga)_5O_{12}$:Tb^{3+} thin films to $Y_2Si_2O_7$:Tb^{3+} by diffusion of Si from the substrate due to high temperature annealing. It is therefore important to develop a better understanding of the kinetics of the film formation, as this may be different for various growth conditions. In order to have a better understanding of the film growth and interfacial reactions, high annealing-temperature studies should be performed to phase separate the possible rapid reactions occurring at high temperatures. Such studies could also reveal pathways for interfacial or bulk film formation, especially for a silicate film. In this work, we report on the high temperature annealing studies of $Y_3(Al,Ga)_5O_{12}$:Tb^{3+} films on Si(1 0 0). Changes in the excitation and emission peaks after annealing were monitored to determine the effect of the Si interdiffusion in the $Y_3(Al,Ga)_5O_{12}$ matrix. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to analyze the changes that occur in the structural properties of the thin films as a result of post deposition annealing.

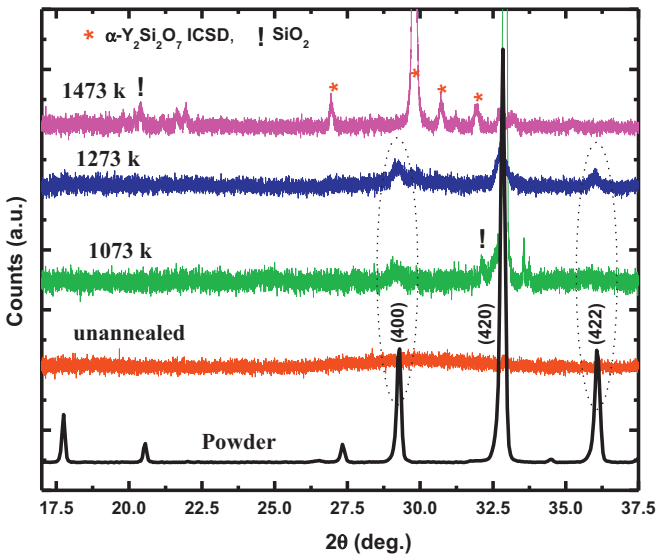

Fig. 1. XRD spectra of $Y_3(Al,Ga)_5O_{12}$:Tb phosphor powder, unannealed and annealed thin films with the standard ICSD data of α-$Y_2Si_2O_7$.

2. Experimental setup

A commercial $Y_3(Al,Ga)_5O_{12}$:Tb powder phosphor, obtained from Phosphor Technology was pressed without binders using an in-house built sample holder and was used as an ablation target. The target was annealed at 873 K for 2 h in air to get rid of all adventitious water containing species that might be present in the pellet and was then placed inside the chamber of the PLD system on a rotating target holder that can also move linearly (up and down). Note that the rotational as well as linear motion of the target rod restricted the laser ablation induced degradation of the target surface. Si(1 0 0) wafers were used as substrates after cleaning with ethanol for 15 min, in an ultrasonic water bath and then blown dry with nitrogen (N_2) gas. The deposition chamber was evacuated to a base pressure of 1.4×10^{-5} mbar and then backfilled with Ar gas to a pressure of 20 mbar. The $Y_3(Al,Ga)_5O_{12}$:Tb target was in the Ar working atmosphere using a 266 nm Nd:YAG 266 pulsed laser. The laser frequency, number of pulses fluency, substrate temperature and target-to-substrate distance were fixed at 10 Hz, 10,000, 0.767 J/cm^2, 573 K and 4.5 cm, respectively. The deposited thin films were annealed in air for 3 hours at a) 1073 K, b) 1273 K and c) 1473 K. X-ray diffraction (XRD) analysis was carried out using a Bruker AXS D8ADVANCE X-ray diffractometer, with a Cu $k_{\alpha 1}$ (1.5406 Å) in the 2θ range from 15°–50°, with a counting time of 1 s for each step size of 0.015°. Photoluminescent (PL) properties of the films were measured using a Carry eclipse spectrophotometer at room temperature excited by mono-chromatized Xenon flash lamp. The surface morphology and roughness were examined from images captured in contact mode using Shimadzu SPM-9600 atomic force microscopy (AFM). The root mean square (RMS) roughnesses were estimated by analyzing the topography scans the films' surfaces using commercial software. The cathodoluminescence (CL) degradation data were collected using Ocean Optics PC2000 spectrometer attached to the vacuum chamber of the PHI 545 Auger electron spectrometer and the data were recorded using OOI Base32 computer software. Thermoluminescence (TL) data were collected with a TL 10091, NUCLEONLX spectrometer and the data were fitted with a TL Glue Curve Analyzer. X-ray photoelectron spectroscopy (XPS) was used to analyze the electronic states of the thin films before and after annealing using a PHI 5000 Versaprobe-Scanning ESCA Microprobe. The survey scans were recorded with a 100 μm, 25 W, 15 kV beam using monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV) and for the higher resolution spectra the hemispherical analyzer pass energy was maintained at 11.8 eV (C1s, O1s, Y3d and Si2p) for 50 cycles. Measurements were performed using either a 1 eV/step and 45 min. acquisition time (binding energies ranging from 0 to 1400 eV) for survey scans or a 0.1 eV/step and 20–30 min acquisition times for the high resolution scans and 90 min. The pressure during acquisition was typically under 1×10^{-8} Torr. MULTIPAK software [12] was used to fit/deconvolute the peaks. Depth profiling experiments were conducted to determine the thicknesses of the films and to obtain information on the variation of chemical composition with the depth below the initial surface. The film surfaces were sputtered using an Ar ion gun (2 kV energy ions) at the rate of about 0.8 nm/min.

3. Result and discussion

3.1. Structural and morphology analysis

Fig. 1 shows the XRD spectra of the $Y_3(Al,Ga)_5O_{12}$ powder, the as deposited and annealed $Y_3(Al,Ga)_5O_{12}$ thin films. The XRD pattern of the powder is consistent with the cubic (Ia-3d(230)) $Y_3(Al,Ga)_5O_{12}$ phase and ICSD data file no. 029248 [13]. No diffraction peaks were observed from the as deposited films suggesting that the film was amorphous. Two diffraction peaks located at 29.32° and 32.82° were obtained from the film annealed at 1073 K, indicating improvement in the film crystal structure. The film was preferentially orientated in the (420) direction. When the annealing temperature was increased to 1273 K three diffraction peaks oriented in the (400), (420) and (422) were obtained. A totally different diffraction pattern was observed when the annealing temperature was increased further to 1473 K indicating that $Y_3(Al,Ga)_5O_{12}$ was converted into new compound(s) at this temperature. The peaks labeled with an asterisk (*) in the spectrum are in agreement with the $Y_2Si_2O_7$ pattern of the ICSD file no. 361476 (DATA) indicating that $Y_2Si_2O_7$ was formed as a result of atomic interdiffusion between the substrate and the film when the films were annealed between 1073 K and 1473 K. An additional new peak marked with an exclamation mark (!) is similar to a diffraction peak from SiO_2.

The surface topography of the as deposited and annealed thin films was studied using atomic force microscopy (AFM). Fig. 2(a) and (b) shows respectively the three dimensional AFM images of the as deposited thin film and the film annealed at 1473 K, which