The influence of working atmosphere on $Y_3(Al,Ga)_5O_{12}$:Tb thin films grown with the PLD technique

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Abstract. $Y_3(Al,Ga)_5O_{12}$:Tb thin films were grown on Si (100) substrates using the pulsed laser deposition technique. The influence of working atmosphere (base pressure, O_2, Ar and N_2) on morphology and structure of the thin films were investigated by Atomic force microscopy (AFM) and X-ray diffraction (XRD), respectively. Auger electron spectroscopy (AES) was employed to analyze the surface chemical composition of the films and the Auger data confirmed the presence of all major elements, namely Yttrium (Y), Aluminum (Al), Gallium (Ga) and Oxygen (O) present in the $Y_3(Al,Ga)_5O_{12}$:Tb phosphor. The brightest emission was observed from the film which was deposited in the O_2 atmosphere, indicating that oxygen is the best working atmosphere for growing the $Y_3(Al,Ga)_5O_{12}$:Tb thin films. AES also shows the differences in atomic concentration of the different films in comparison with that of the phosphor powder. The concentration of the elements of the O_2 atmosphere thin film was more similar to the elemental concentration of the powder itself.

1. Introduction

Pulsed laser deposition is a widely used technique to grow thin films for a variety of applications. The major advantage of the Pulsed Laser Deposition (PLD) is the ability to transfer the material stoichiometry from a multi-component ablation target to a growing film [1-3]. However, it is well known that such favourable results do not occur under all experimental conditions. Therefore different deposition parameters for each kind of material need to be optimized to get the films with the desired properties. Parameters that may play a role are target-substrate distance, different working atmosphere, substrate temperature, laser pulse energy density and pulse repetition rate [2, 4]. Compared to powders that are widely used in conventional displays, thin phosphor films have advantages such as superior thermal conductivity, a high degree of uniformity, a better thermal adhesion to the substrate. In addition, the uniform thickness combined with smoother surface morphology and smaller grain size makes it possible to obtain smaller pixel spot size for achieving higher resolution [5]. Yttrium aluminium garnet $Y_3Al_5O_{12}$ material has been widely studied for different applications, by changing the dopants, the materials can be used to produce phosphors for a full-color display. It can withstand a high-energy electron beam and has been considered as an ideal candidate to prepare display phosphors

[6,7]. The brightness and the saturation characteristics of $Y_3Al_5O_{12}$:Tb were improved by the replacement of a portion of Al with Ga resulting in a $Y_3(Al,Ga)_5O_{12}$:Tb phosphor, that shows very good cathodoluminescent (CL) stability, during prolonged electron bombardment, indicating that, it is a promising phosphor candidate for field emission displays (FEDs) or other light emitting devices [7]. Thin films of $Y_3Al_5O_{12}$:Tb phosphor have already been fabricated by the PLD technique and has been proposed for practical application [1] but there are no reports on $Y_3(Al,Ga)_5O_{12}$:Tb thin films fabricated by PLD. In this study all the deposition parameters were kept constant except the working atmosphere. The working atmospheres used were base pressure, oxygen, and argon and nitrogen pressures.

2. Experiment

Phosphor powder of $Y_3(Al,Ga)_5O_{12}$:Tb, obtained from Phosphor Technology [8] was directly pressed without binders into a homemade sample holder and was used as an ablation target. The target was annealed at 600 ^oC for 2 hrs in air and was then placed inside the PLD system on a rotating target holder. Si (100) wafers were ultrasonically cleaned sequentially in ethanol for 15 min, were transferred to an ultrasonic water bath and then dry blown with nitrogen (N_2) gas. The films deposited in the different gas atmospheres were then deposited after the deposition chamber was evacuated to a base pressure of 1.4×10^{-6} m bar and then backfilled to a deposition pressure of 2.7×10^{-2} m bar for each gas (O_2, N_2 and Ar), except for the film deposited at the base pressure, where the chamber pressure was 6.6×10^{-6} m bar during the deposition process. A Nd:YAG 266 nm pulsed laser was used to ablate the phosphor pellet in the different working atmosphere. The laser frequency and fluence were 10 Hz and 0.767 J/cm^2 respectively. The substrate temperature was fixed at 400 ^oC and the target to substrate distance was 6 cm. X-ray diffraction (XRD) analysis was carried out using a Bruker AXS D8ADVANCE diffractometer, using a Cu K_α (1.5406 Å) radiation in the 2θ range from 15^o–50^o, with a counting time of 1 s for each step size of 0.015^o. Photoluminescent (PL) properties of the thin films were measured using a Carry eclipse spectrophotometer at room temperature using a monochromatized Xenon flash lamp as an excitation source. The surface morphology and roughness were examined by atomic force microscopy (AFM) with a Shimadzu SPM-9600 set in contact mode. The root mean square (RMS) roughness values were calculated from the height values from the AFM images using commercially available software. Chemical composition analyses and depth profiles were carried out using a PHI 700 nano scanning Auger electron microprobe (NanoSAM), surveys were done with 25 kV 10 nA electron beam, a 2 kV Ar ion gun was used and the sputtering rate was 27 nm/min.

3. Results and discussion

3.1 Structural, morphology and chemical composition analysis

Figure 1 shows the XRD patterns of $Y_3(Al,Ga)_5O_{12}$:Tb powder and the films grown in the different working atmospheres. For the films prepared at base pressure and in Ar and N_2 broad diffraction peaks located at 2θ=29.55^o were observed, indicating that amorphous structures were formed during the deposition process. The XRD from the O_2 layer only shows the (420) peak of $Y_3(Al,Ga)_5O_{12}$ [7] and peaks which are labelled with an asterisk (*) can be associated with diffraction from the Si substrate. The deposition layer therefore has a 420 preferential orientation. The substrate peaks are not consistent but have been obtained in several other measurements in the past. The XRD of the Ar sample also has a (420) peak. Jiwei et al. [9], Jong-Ho Park et al. [11] and Naohiro et al. [12] reported that some peaks of the Y_2O_3:Tb cubic structure are in the range of these broad peaks.

Figure 2(a)-(d) shows three dimensional AFM images of the films. The film grown in base pressure in Figure 2 (a) shows undefined grain boundaries and a uniform surface with root mean square (RMS) roughness around 6 nm. The RMS was calculated without inserting the larger defect in the surface that can be seen in the figure. On the contrary, Figure 2 (b) presents the surface of the film grown in the O_2 atmosphere, where big agglomerated grains with defined grain boundaries and roughness of about 30 nm were obtained. Figure 2(c) exhibits the surface topography of the Ar

atmosphere thin film showing a smooth surface between spaced bigger grains with roughness of about 12 nm. The roughness of the N_2 film shown in Figure 2 (d), is about 5 nm with a well defined grain distribution but it seems that the film was not continuous. It can be concluded that the surface roughness, grain shape and size were influenced by the deposition environment.

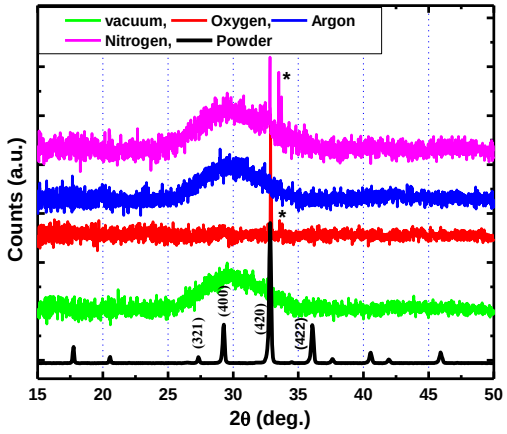

Figure 1. XRD spectra of $Y_3(Al,Ga)_5O_{12}$:Tb phosphor powder and thin films grown in different working atmosphere.

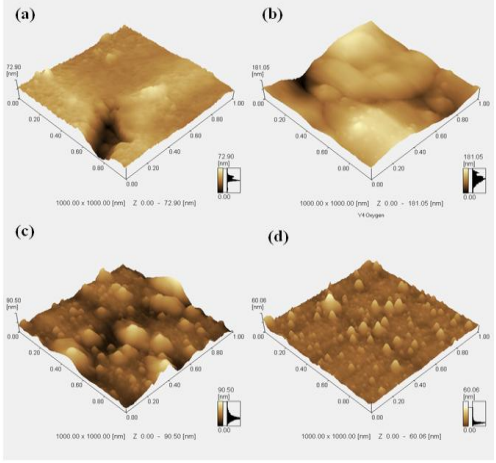

Figure 2. Three dimensional AFM images, for the thin film surfaces, grown in (a) base, (b) O_2, (c) Ar and (d) N_2 atmosphere.

The surface morphology of the films prepared in the different working atmosphere, can be seen from the SEM images in Figure 3(a)-(d). Figure 4 (a)-(i) show the AES spectra of (1) the $Y_3(Al,Ga)_5O_{12}$:Tb powder (2-4) the thin films that were grown in base pressure, (5) O_2, (6) Ar and (7) N_2 pressure. The spectra were recorded at the indicated positions on the SEM images. Spherical particles appeared on the smooth surface of the $Y_3(Al,Ga)_5O_{12}$:Tb films. Some areas of the substrate's surface were not completely covered with the thin film that was prepared in base pressure, Figure 4 (a). It can probably be referred to as the Volmer–Weber growth mode [13] where the energy due to the creation of interface is higher than the surface energy of the substrate and film. On the contrary, all the other substrate surfaces were covered with the deposited material for the films that were grown in (b) O_2, (c) Ar and (d) N_2. The AES spectra in Figure 4 confirm the presence of all the major elements, namely Yttrium (Y), Aluminium (Al), Gallium (Ga) and Oxygen (O) in the $Y_3(Al,Ga)_5O_{12}$:Tb phosphor target and in the thin films [1,7].

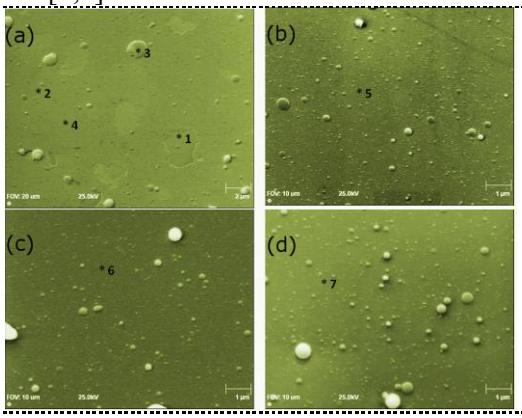

Figure 3. SEM images, for the thin film surfaces, grown in (a) base, (b) O_2, (c)Ar and (d) N_2 pressure.

Figure 5 (a)-(d) show the compositional depth profiles of the thin film layers grown at (a) base pressure, (b) in O_2, (c) in Ar and (d) in N_2. The difference in atomic concentration, of films deposited in the different atmospheres, of each chemical element determined from the middle of the films is presented in table 1. The film grown in the O_2 atmosphere is enriched in oxygen with respect to the films grown at the base, Ar and N_2 atmospheres. It seems that during transport of the ablation material a depletion of some of the oxygen occurred. In the presence of the O_2 atmosphere, however, some of these are replaced leading to a thin film stoichiometry that is most similar to the original phosphor as shown in figure 6 and table 1. The thickness of the films were determined from the AES depth profiles to be approximately 55, 45, 40 and 30 nm for the films prepared in the base pressure, O_2, Ar and N_2 atmospheres respectively.

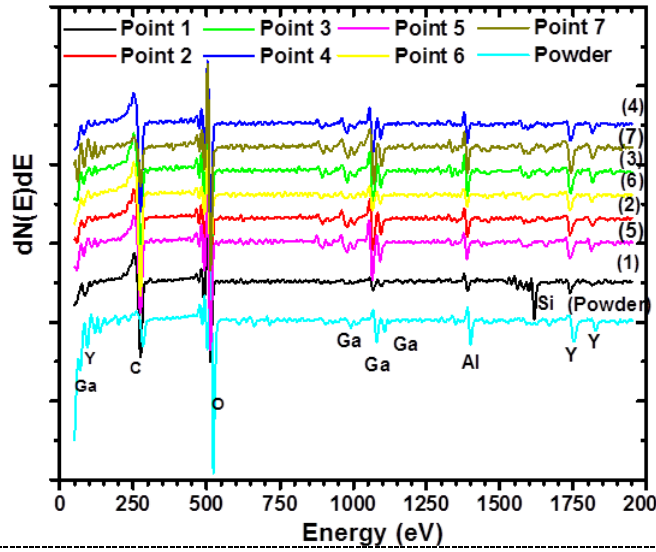

Figure 4. Different AES spectra of $Y_3(Al,Ga)_5O_{12}$:Tb powder (a) and thin films grown in base pressure (b-e), (f) O_2, (g)Ar and (i) N_2 atmospheres.

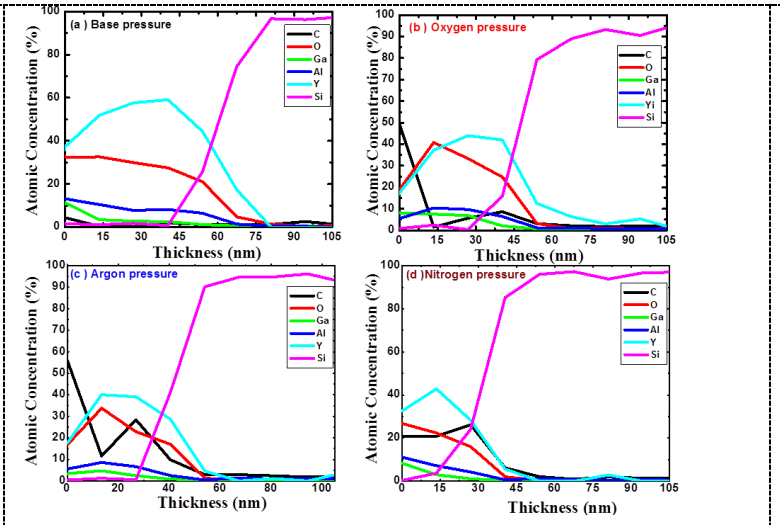

Figure 5. Depth profiles of the thin films structures, that were grown in (a) base, (b) O_2, (c) Ar and (d) N_2 atmospheres.

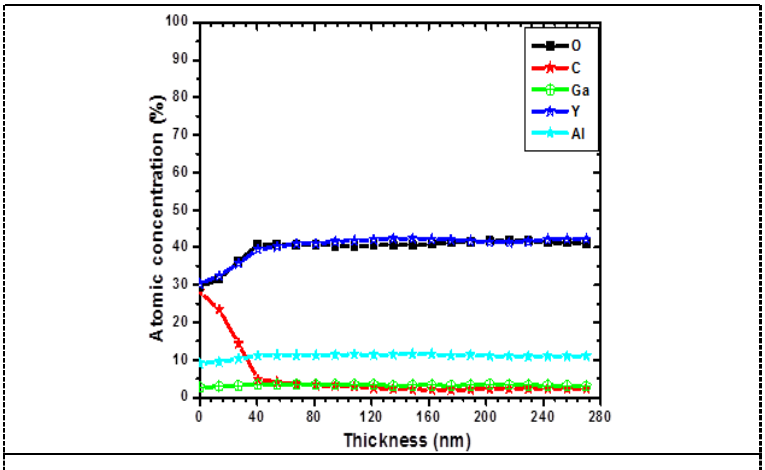

Figure 6. Depth profile of the phosphor powder.

3.2 Photoluminescence (PL)

The PL emission characteristics for the thin films are illustrated in Figure 7. They all show typical emission spectra of Tb^{3+} ions due to the 5d-4f transitions from the excited $^5D_4$ level to ^5F_j (j=6-4) levels of the ground state with the main peak at a wavelength of 544 nm ($^5D_4 \rightarrow {}^7F_5$) and minor peaks at 489 nm ($^5D_4 \rightarrow {}^7F_6$), 561 nm ($^5D_4 \rightarrow {}^7F_4$) and 625 nm ($^5D_4 \rightarrow {}^7F_3$) [7,10]. The effect of different working atmosphere on the intensity can clearly be noticed in Figure 7. The highest luminescent emission intensity was obtained from the thin film grown in the O_2 working atmosphere.

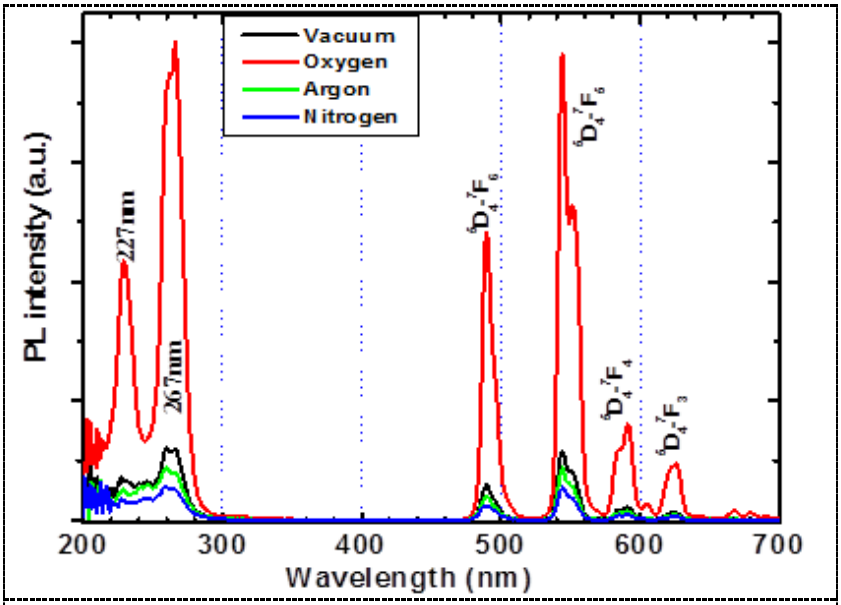

Figure 7. PL emission and excitation of $Y_3(Al,Ga)_5O_{12}$:Tb thin films grown in different working atmosphere (Excitation measured at an emission wavelength of 544 nm; emission measured at an excitation wavelength of 267 nm).

Table 1: Atomic concentrations determined from the middle of the thin film layers deposited in the different working atmosphere

Working atmosphere	Atomic concentrations (%) at middle of the thin film layers					
	O	Y	Al	Ga	C	Si
Base pressure	30	57	8	3	0.2	1.5
Oxygen	37	40	10	7	4	1
Argon	28	40	7	4	20	1
Nitrogen	23	41	8	3	21	3
Powder	42	40	12	4	2	

4. Conclusion

Our results show that there is a clear correlation among the deposition atmosphere, structural properties of the thin films and their luminescent properties. The highest luminescent emission intensity was obtained from the film grown in the O_2 working atmosphere. Deposition in vacuum gives a smoother surface with roughness value around 6 nm and deposition in oxygen gave big agglomerated grains with defined grain boundaries and roughness of about 30 nm.

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