YVO_4:Eu phosphors thin films prepared by PLD

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Abstract. Yttrium vanadate doped europium (YVO_4:Eu) phosphor thin films were deposited on silicon substrates using the pulse laser deposition technique. The films were deposited at room temperature with different O_2 pressures of 20, 100 and 200 mTorr. The X-ray diffraction patterns of the films deposited at 100 mTorr exhibits a strong preferential orientation in the (200) direction. The thin films showed a rough surface and large number of spherical particles at a higher O_2 pressure than that of the lower O_2 pressure. Luminescence of the YVO_4:Eu showed a strong red emission peak at 618 nm due to the $^5D_0$-$^7F_2$ transition.

1. Introduction

Oxide thin film phosphors have been given attention because of its high resolution and high efficiency planar display. The oxide based phosphors appeared as a potential choice for the red field emission display (FED) phosphor. The luminescence efficiency of most phosphor materials is affected by the concentration of the activator. YVO_4:Eu^{3+} thin films is one of the most promising oxide-based red phosphor with application in high pressure mercury lamps, television cathode ray tube displays but mostly in plasma display panels [1,2]. YVO_4 has a body centered tetragonal structure that consists of four formula units in a unit Cell with lattice parameters of α=0.71192 and c=0.62898 nm [3]. Thin films has been prepared by many other deposition techniques, such as spray pyrolysis, chemical vapor deposition (CVD), Molecular beam epitaxy (MBE) or vacuum deposition [4]. These methods showed a lack of crystallographic orientation control or an enrich nonstoichiometric phase [5]. Thin films of YVO_4:Eu^{3+} have been prepared by pulse laser deposition (PLD). PLD is known as a unique process that provides stoichiometric transfer of target materials. This technique allows thin films deposition of good quality films at low temperatures. The factors that can influence the brightness of the thin film phosphors can be the crystallinity, morphology and surface roughness [6]. This is an attractive method for growing high-quality crystalline films because it is cheap, simple and a reliable technique. In this work the structural characteristics and photoluminescence (PL) properties of YVO_4:Eu films prepared by PLD were investigated.

2. Experimental

Commercial YVO_4:Eu phosphor powder was purchased from phosphor technology. Targets for PLD were prepared from YVO_4:Eu powder by cold-pressing followed by sintering for 2 hours at 800 ^oC in air. YVO_4:Eu thin films were deposited on Si substrate with typical size of 25 x 25 mm^2 at room temperature using a frequency tripled Nd:YAG Laser. The laser pulse of 10 Hz was focused onto the rotating target and the energy laser was approximately 47 J/cm^2. The distance between the target and the substrate was kept constant at 45 mm during the deposition of each film. The films were deposited at different oxygen background pressures of 20 mTorr, 100 mTorr and 200 mTorr at room temperature.

The characterization of the films structure and phase identification was carried out with x-ray diffraction (XRD). Morphologies of the films were obtained using a scanning electron microscope (SEM) and Atomic force microscopy (AFM) micrographs were obtained with the Shimadzu SPM – 96 model. PL data were recorded with a Cary Eclipse Fluorescence spectrophotometer.

3. Results and discussion

3.1 Structure and morphology

Figure 1 shows the XRD patterns of the YVO_4:Eu powder and thin films deposited on the Si substrate at room temperature for different O_2 pressures of 20 mTorr, 100 mTorr and 200 mTorr. All the peaks of the powder are matched well with the tetragonal phase (JCPS Card 17-341) and no second phase was observed. Compared with XRD pattern of polycrystalline YVO_4:Eu phosphor powder used as a target, most peaks in all films are broadened most probably due to small particle size but still could be indexed on tetragonal YVO_4:Eu phase. It was observed that the crystallization improves with an increase in the oxygen deposition pressure. Films deposited at low pressure of 20 mTorr display a single peak along the (200) direction. The films grown at O_2 pressure of 100 mTorr depict high intensity peak at (200) and a second low intensity one along (400) showing relativity well-preferred orientation of (200) plane. When the growth O_2 pressure increased to 200 mTorr the film showed diffraction peaks at (200) and (112), indicating that there is no predominantly preferential growing orientation at the present films condition.

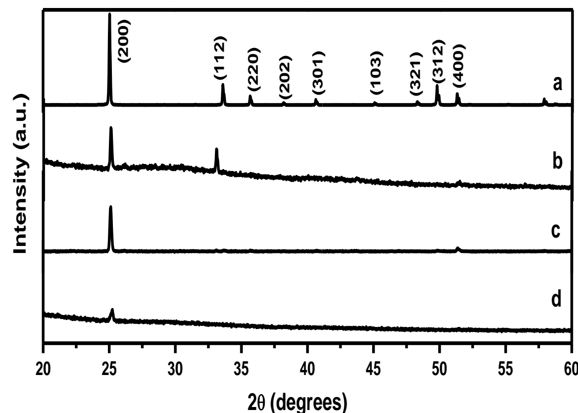

Figure 1: XRD patterns of YVO_4:Eu (a) powder, and thin films deposited at (b) 200m Torr (c) 100 mTorr (d) 20mTorr at room temperature.

AFM images of YVO_4:Eu thin films deposited in room temperature at varying O_2 Pressure in the range of 20 – 200 mTorr are shown in figure 2. It can be observed from the results that different morphologies were obtained by changing the O_2 pressure during deposition. It is clear that the particle sizes of the films deposited at higher O_2 pressure were much larger than that of the films deposited at lower O_2 pressure suggesting that the growth rate of deposited particles was much faster at higher O_2 pressure. The increase in crystallite size possibly results from the enhancement of the film surface atomic mobility with abundance of oxygen species, which enables the thermodynamically favored grains to grow. The films deposited at lower O_2 pressure of 20 mTorr had smoother surfaces than the film deposited at higher O_2 pressure. The surface topography changed from smooth to nodular with an increase in O_2 pressure. Increasing the O_2 pressure to 100 mTorr yielded a complete development of nodular surface with well defined grain boundaries. Further increase of the oxygen pressure to 200

mTorr resulted into a well-developed nodule surface with slightly less rough surface but well defined edges are obtained as compared to the films deposited at O_2 pressure of 100 mTorr.

Figure 3 shows the SEM micrographs of YVO_4:Eu films grown on Si substrate at room temperature during 27000 pulses. The SEM pictures confirm that the surfaces of the films prepared at higher oxygen pressure are much rougher and particles much larger than that deposited at low O_2 pressure. The film deposited in 20 mTorr O_2 pressures, shown in figure 3(a), had smooth surface with small nearly spherical particles and the bigger particles at some regions are due to spitting. Film deposited at O_2 pressure of 100 mTorr had a rougher surface also with bigger spherical particles as shown in figure 3(b) but with no developed edges. The results shows that the film deposited in higher oxygen pressure of 200 mTorr had also rougher surface packed with nearly O_2 particles with well developed straight edges. The SEM pictures shows that increasing the oxygen pressure results into the increase surface roughness and this maybe due to the enhanced particulate formation in plume, which is characteristic of high pressure ablation [7].

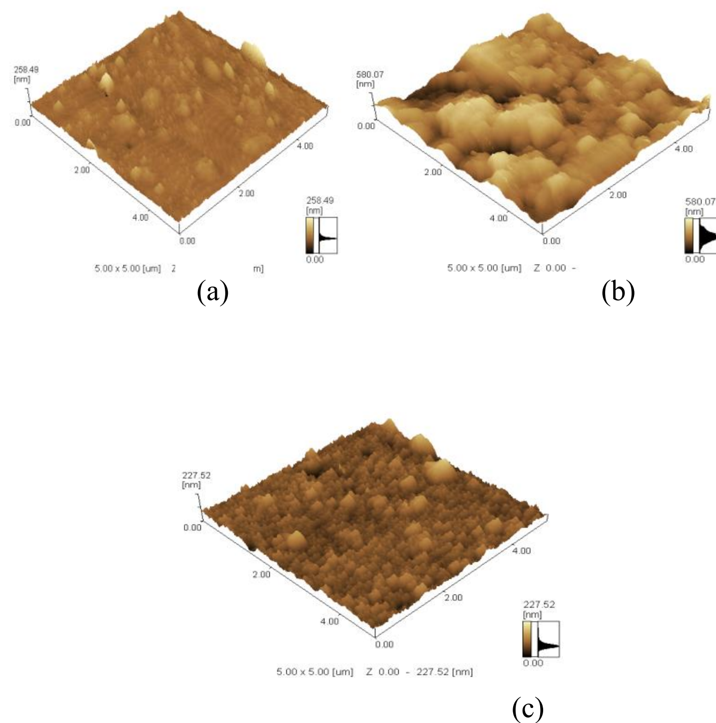

Figure 2: AFM images of YVO_4:Eu thin films deposited on Si substrates at O_2 pressures of (a) 20 mTorr (b) 100 mTorr and (c) 200 mTorr.

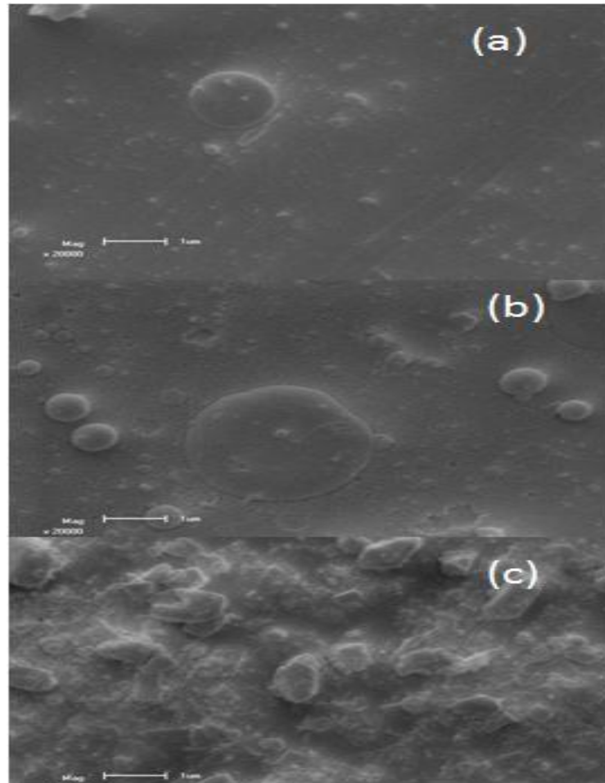

Figure 3: SEM images of $Eu:YVO_4$ thin films deposited on Si substrate at (a) 20, (b) 100 and (c) 200 mTorr O_2 pressure.

3.2 Photoluminescence characteristics

Figure 4 shows the excitation spectra of YVO_4:Eu thin films deposited at room temperature with different O_2 pressure as well as the phosphor powder. The excitation spectra monitored with 618 nm emission of Eu^{3+} ($^5D_0$-$^7F_2$) consists of a strong absorption band from 200 nm to 340 nm with a median maximum at 275 nm due to the VO_4^{3-} ion. Obviously, this band is ascribed to a charge transfer from the oxygen ligands to the central vanadium atom within the VO_4^{3-} group ions [7]. From the viewpoint of molecular orbital theory, it corresponds to transitions from the $^1A_2$ ($^1T_1$) ground state to $^1A_1$ (^1E) and ^1E ($^1T_2$) excited states of VO_4^{3-} ion [8]. The general f-f transition lines of Eu^{3+} in the longer wavelength region have not been observed due to their weak intensity relative to that of the VO_4^{3-}. This indicates that the excitation of Eu^{3+} is mainly through the VO_4^{3-} ions, i.e., by energy transfer from VO_4^{3-} to Eu^{3+} [9]. The excitation intensity of the films increases with an increase in the O_2 pressure. This means that the energy transfer from host YVO_4 to Eu^{3+} is gradually enhanced. The PL emission spectra of YVO_4:Eu phosphor in figure 5 show a considerable number of lines between 575 and 725 nm, representing the transitions $^5D_0$-^7F_J between the first excited states and the ground multiple of the Eu^{3+}. YVO_4:Eu showed a strong red emission peaks at 618 nm assigned to $^5D_0$-$^7F_2$ transition. Other peaks at 594 nm, 650 nm and 699 nm represent the transitions at $^5D_0$-$^7F_1$, $^5D_0$-$^7F_3$ and $^5D_0$-$^7F_4$ respectively. No emission from the VO_4^{3-} group is observed, suggesting that the energy transfer from VO_4^{3-} to Eu^{3+} is very efficient. The PL spectra of films show some differences with oxygen pressure, and the intensity of PL in films is relatively weak compared with the powder. As the O_2 pressure increased from 20m Torr to 100 mTorr the PL intensity did not show much difference but increased significantly as the oxygen growth O_2 pressure increased to 200 mTorr (Fig. 4(d)). The $^5D_0$-^7F_J emission is very suitable to survey the environmental effects on the sites of Eu^{3+} ion in a host lattice without inversion symmetry such as YVO_4 [10]. While the $^5D_0$-$^7F_4$ transition is sensitive to long range environmental effects, the $^5D_0$-$^7F_2$ transition which originates from interactions with neighbours is hypersensitive to, especially short-range, environmental effects. However, the $^5D_0$-$^7F_1$, the allowed magnetic-dipole transition, is

not affected by the Eu^{3+} ion so that it is usually utilized as an internal standard. The similar intensity ratios of $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_4$ transitions to $^5D_0$-$^7F_1$ transition in PL spectrum of YVO_4:Eu represent that Eu^{3+} ions are occupied in yttrium sites of YVO_4 lattice and the long-range environments of Eu^{3+} ions in the film are not much different from powder. This indicates that YVO_4:Eu film deposited by PLD is well crystallized even without any post-annealing. The dependence of PL emission on the deposition O_2 pressure is shown in insertion graph in Figure 5.

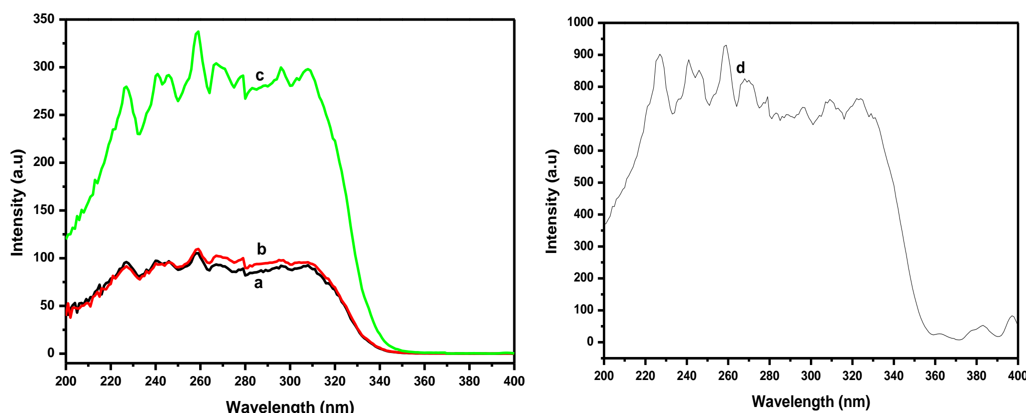

Figure 4: PL excitation spectra of Eu:YVO_4 thin films deposited on Si substrate at (a) 20, (b) 100 and (c) 200 mTorr and powder (d).

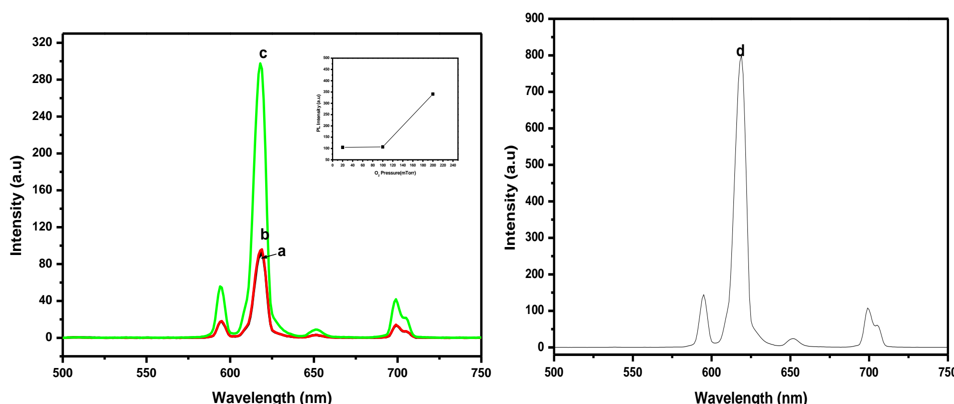

Figure 5: PL emission spectra of YVO_4:Eu thin films deposited on Si substrate at (a) 20, (b) 100 and (c) 200 mTorr and (d)Powder

4. Conclusion

YVO_4:Eu thin film phosphors have been deposited on Si substrates using PLD. The surface roughness of the films was highly depends on oxygen pressure. The films deposited at lower O_2 pressure of 20 mTorr had smoother surfaces than the film deposited at higher O_2 pressure. The SEM images confirm that the surfaces of the films prepared at higher O_2 pressure are much rougher and particles are much larger than that deposited at low O_2 pressure. The XRD patterns of phosphor powder showed the tetragonal single phase. Thin films peaks are broadened and most probably due to small particle size but still could be indexed on tetragonal YVO_4:Eu phase. PL emission spectra showed a red emission peak at 618 nm which assigned to $^5D_0$-$^7F_2$ transition. The PL intensity has increased when the O_2 pressure increased to 200 mTorr.

Acknowledgment
The authors send gratitude to the National Research Foundation (NRF) for funding the project and the University of Free State Physics (Physics department) for the research techniques used in this study.

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