The effect of substrate temperature on the structure, morphology and photoluminescence properties of pulsed laser deposited $Y_3(Al, Ga)_5O_{12}:Ce^{3+}$ nano thin films.

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Abstract. Luminescent properties of $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ thin films were studied. $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ phosphor powder was used as target material for Pulsed Laser Deposition of the thin films at different substrate temperatures in an O_2 background atmosphere. X-ray diffraction indicated that the films have the same cubic polycrystalline phase structure as the powder. Atomic force microscopy revealed poorly defined grain growth for films ablated at a substrate temperature of 22°C and 500°C but well defined grain growth was observed for films ablated at a 300°C substrate temperature. Auger electron spectroscopy depth profile of the film ablated at 500°C indicated that Si has diffused into the thin film. The highest photoluminescent (PL) intensity was observed for films deposited at the substrate temperature of 300°C. A slight shift in the wavelength of the PL spectra was obtained for the thin films with respect to the powder due to a change in the crystal field.

Introduction

$Y_3Al_5O_{12}:Ce^{3+}$ or YAG:Ce is used in several applications such as solid state lighting and displays. When Ga is added and substituted for Al to form Y_3 $(Al,Ga)_5O_{12}:Ce^{3+}$, this phosphor has the potential to be applied in the fabrication of Light emitting diodes especially if the phosphor is used in the thin film form. Thin films offers several advantages due to their good luminescence characteristics, higher image resolution from small grains, better thermal stability and good adhesion to the substrate [1]. The substrate temperature plays a critical role in the growth of the films during the Pulsed Laser Deposition (PLD). The mobility of the atoms deposited on the surface is directly dependent on the temperature of the substrate. The activation energy of processes that takes place on the surface is influenced by this dependency [2]. The movement and interaction on the surface of the substrate of different particles (atoms, ions, electrons etc.) that makes up the plume is mainly determined by the substrate temperature and the energy of these deposited particles [3]. The crystallinity of the as-grown films has been shown to be highly dependent on the processing temperature [4]. Research on the influence of substrate temperature on $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ thin films is of great importance to establish the optimum substrate temperature range for a high photoluminescence (PL) intensity. In this paper we report on the luminescence and morphological properties of $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ thin films prepared by PLD. The aim was to establish the optimum substrate temperature that will produced thin films with a

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high PL intensity as well as structural properties similar to the $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ phosphor in the powder form.

Experimental Setup

$Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ powder phosphor obtained from Phosphor Technology (UK) with Commission Internationale de l'Eclairage (CIE) coordinates: (x=0.306, y=0.521) and non-uniform particles with median particle size of 2.5 µm were used in this study [5]. The Ga to Al ratio is about 60:40 in the $Y_3(A,Ga)_5O_{12}:Ce^{3+}$ crystal structure. The powder was pressed without binders to make a pellet which was used as a target for PLD. Si (100) wafers were used as substrates. They were cut into approximately 2 cm by 2 cm pieces and cleaned in an acetone ultrasonic bath for 15 minutes. A layer of SiO_2 was grown on some of the Si substrates. The phosphor target and one Si piece at a time were inserted into the PLD chamber. An Nd:YAG 266 nm laser was used for the deposition. The laser fluency was kept at 0.78 J/cm^2 with a 10 Hz frequency. The target to substrate distance was kept at 6 cm. The chamber was evacuated to a base pressure of 3.7×10^{-6} torr. Then the chamber was backfilled with O_2 gas to a chamber pressure of 1×10^{-2} torr. The ablation was performed for substrate temperatures of 22°C, 100°C, 300°C and 500°C. The room temperature samples were deposited on the Si(100) without SiO_2, while the higher temperature samples were deposited on the Si/SiO_2 substrates. The films were then annealed at 800°C for 2 hours in open air. Atomic Force Microscopy (AFM) was used to obtain micrographs of the surface using the Shimadzu SPM – 9600 model. PL excitation and emission spectra ware recorded using a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) at room temperature using a 140 W monochromatized Xenon flash lamp as an excitation source. X-Ray Diffraction (XRD) data was collected by using a D5000 diffractometer using CuKα radiation of $\lambda = 1.5405$ nm in the 2θ range from 24° – 40°, with a counting time of 2 s for each step size of 0.0302°. Auger Electron Spectroscopy (AES)'s depth profiles and AES survey test of the surface where performed using a PHI 700 Scanning Auger Nanoprobe. AES surveys were done with a 25 kV 10 nA electron beam. Depth profiles were done by sputtering with a 2 kV, 2 µA ion beam, at 1x1 mm raster area with a sputter rate of 27 nm per min. Scanning Electron Microscope (SEM) images were obtained with a 25 kV, 10 nA electron beam. Line profiles were done with a 25 kV, 10 nA electron beam.

Results

Figure 1 shows the XRD patterns of the films ablated at different substrate temperatures together with the powder pattern. The ICSD file number 29250 is also shown. Crystalline thin films with the same cubic polycrystalline phase structure as the powder were obtained during the PLD. XRD results show a constraint in the growth of the crystals due to a low atomic mobility at a deposited temperature of 22°C. An increase to 100°C and 300°C supplied the atoms on the substrate surface with more thermal energy and thus increased their surface mobility that lead to better crystallization at the higher temperatures. However too high temperatures such as 500°C can decrease the crystallinity of the thin films due to interdiffusion, desorption or dissociation of atoms and molecules.

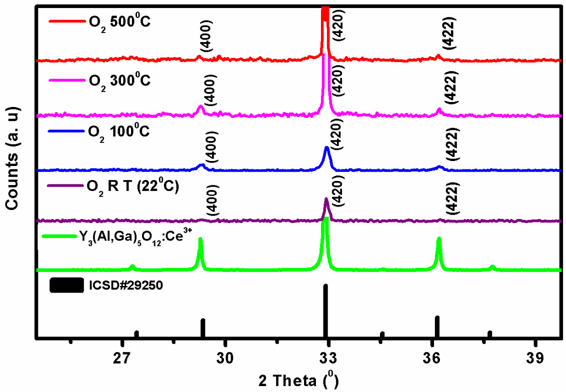

Figure 1. XRD patterns of $Y_3(A,Ga)_5O_{12}:Ce^{3+}$ powder and films deposited at different substrate temperatures.

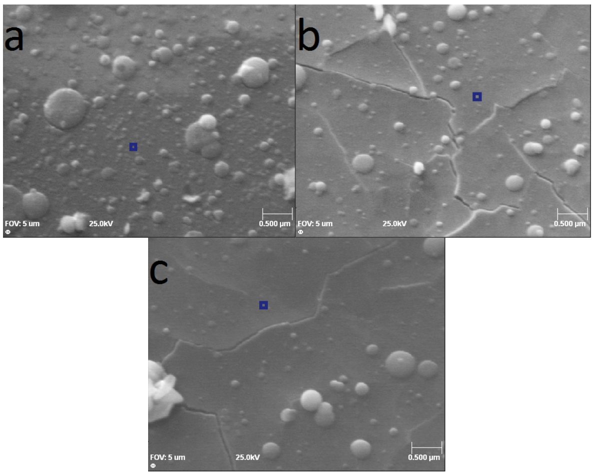

Figure 2. SEM images of films ablated at substrate temperatures of (a) 22°C, (b) 300°C and (c) 500°C.

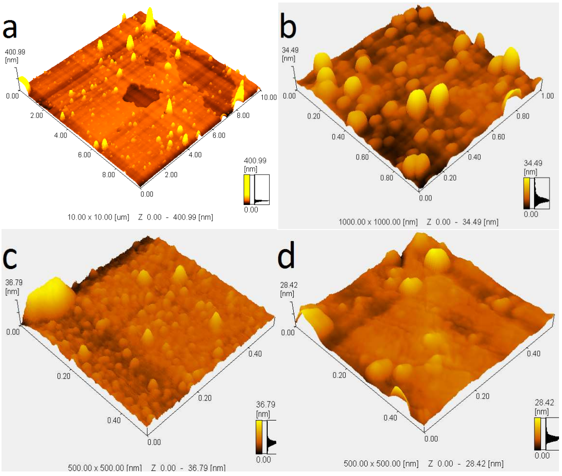

Figure 3. AFM images of films ablated at substrate temperatures of (a) 22°C, (b) 100°C (c) 300°C and (d) 500°C

Effects of substrate temperature on the morphological properties of $Y_3(Al,Ga)_5O_{12}$:Ce^{3+} thin films are shown in Figure 2 and Figure 3. For a substrate temperature of 300°C, a well-defined grain growth is obtained seen on the AFM image in Figure 3(c). A lack of uniformity is observed for films ablated at 22°C (Figure 2(a) and Figure 3(a)) where big and small particles are seen due to the low mobility of the atoms on the surface of the substrate. Figure 3(b) shows a better grain growth but with big and small particles still seen. A poor defined grain growth resulted for films ablated for a substrate temperature of 500°C. For these films shown in Figure 2 (c) and 3 (d), the surface appears melted with a decreased in surface roughness due to the high substrate temperature.

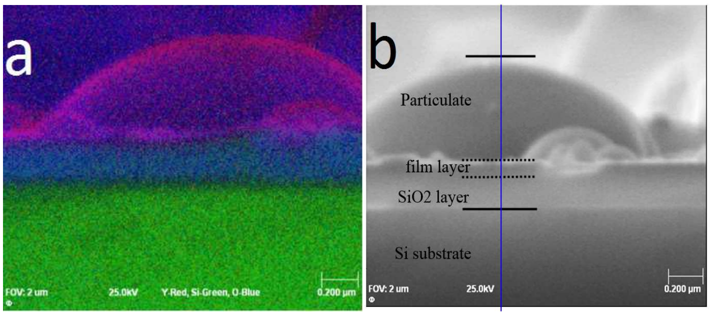

Figure 4. (a) Cross sectional SAM image and (b) cross sectional SEM images of the film ablated at a substrate temperatures of 300°C.

Figure 4 (a) and (b) show a typical cross sectional SAM image and (b) cross sectional SEM image of the film ablated at a substrate temperatures of 300°C. Different regions and layers are indicated by solid and dotted lines on the cross sectional SEM image. It is clear that the deposited film consist of a homogenous thin film and additional big particulates of several hundred nanometer on top of the film. The uniform phosphor layer thickness was estimated at about 160 nm. Similar images were obtained for the other films. The generation of particulates during the deposition process, is not ideal for the application field and is one of PLD's disadvantages. However Coetsee et al. [11] pointed out that these particulates may have an advantage due to the higher CL intensity coming from these particles on the thin film. During the investigation of the CL intensity degradation of tin oxide coated Y_2SiO_5:Ce thin films grown by PLD it was observed that more photons exiting these spherically shaped particles in comparison with the uniform thin layer where the photon get totally internally reflected [11]. The depth profiles were performed at the positions on the surface (indicated by the blue squares in the SEM images in Figure 2) between these big particles and are shown in Figure 5.

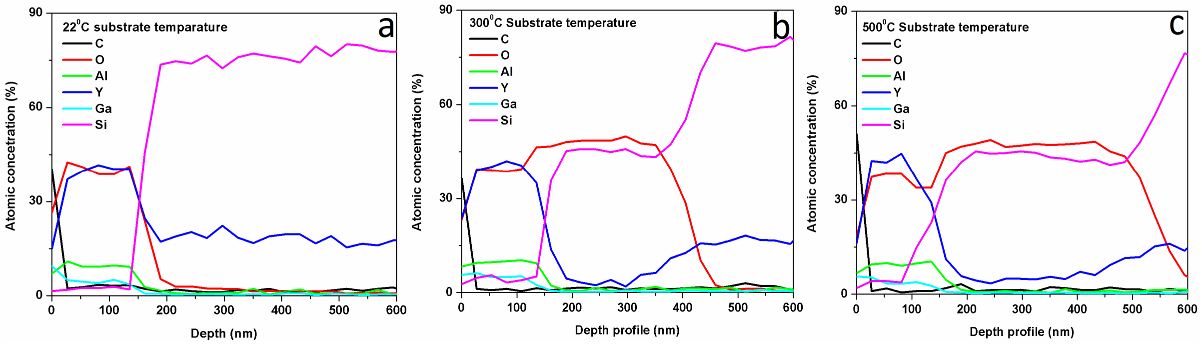

Figure 5. Depth profiles performed of the different substrate temperature films.

Figure 5 shows depth profiles of the films deposited at (a) 22°C, (b) 300°C and (c) 500°C. The depth profiles are from the $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ thin films and the SiO_2 on top of the substrates. A much higher Y concentration as expected were obtained at all the substrate temperatures. By using the point (depth) where the Y concentration is about 50% of the maximum Y concentration as an estimation of the film thicknesses for the 22°C, 300°C and 500°C prepared layers, the thicknesses were determined as 152 nm, 153 nm and 144 nm respectively. Similar thickness values were also found for cross sectional measurements of the films. All the films seem to have almost the same thickness and substrate temperature does not have a significant effect on this regard. The concentration of the elements making up the films also remain more or less the same as the substrate temperature is varied. Please note that Y is not actually diffusing into the SiO_2 layer as observed on the depth profiles. What is seen as Y concentration increasing inside the SiO_2 layer is actually as a result of the Si 1739 eV peak from SiO_2 monitored overlapping with the Y 1748 eV peak and need to be removed in future studies. The distribution of elements, however, is significantly affected at the interface of the phosphor/SiO_2 at the higher substrate temperature during deposition as indicated by the depth profile of the film deposited at the 500°C substrate temperature (Figure 5 (c)). It can be seen that the Si has diffused into the phosphor thin film with the consequent broadening of the interface. The 500°C substrate temperature seems to promote this diffusion of Si into the phosphor thin film layer.

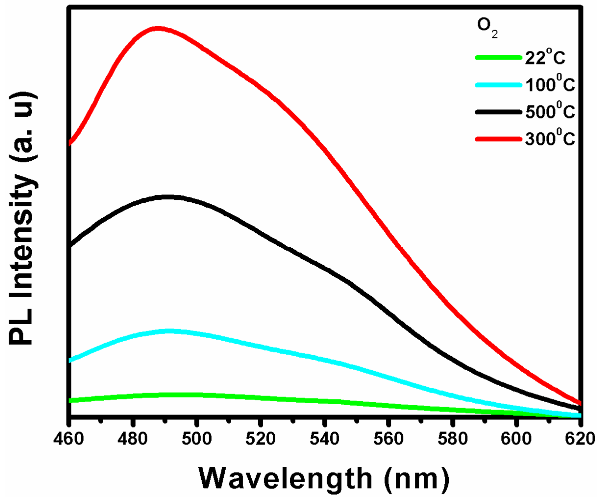

Figure 6. PL intensity of the films deposited in 1×10^{-2} torr O_2 at various substrate temperatures.

$Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ in powder form has 60% Ga and 40% Al, this results in the PL emission wavelength of 512 nm and 565 nm [6]. Figure 6 shows the PL emission of $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ thin films which peaks at around 495 nm and 542 nm. This wavelength shift can be attributed to the change in Ga/Al ratio within the crystal lattice which primarily affects the crystal field around the Ce ion which is responsible for the emission. Ce^{3+} doped phosphors typically have two emission bands due to the true levels of $^2F_{5/2}$ and $^2F_{7/2}$ of the configuration of Ce^{3+} [9, 10]. Each Ce^{3+} site gives rise to transitions from the 5d to the two (therefore two peaks) 4f energy levels ($^2F_{5/2}$ and $^2F_{7/2}$ due to crystal field splitting). The substitution of Ga into the $Y_3Al_5O_{12}:Ce^{3+}$ lattice result in a decompression of oxygen atoms directly coordinated to the Ce^{3+} ion and the structure becomes more cubic. This change in structure directly affects the 5d orbitals of the Ce^{3+} as it moves it from the bottom of the conduction band and likewise the PL characteristics as seen by the shift in Figure 6 [7]. It can also be seen from Figure 6 that the PL intensity increased with an increasing substrate temperature up to 300 °C. Substrate temperature improved the crystallinity and luminescent intensities of thin film phosphors. Interdiffusion of the Si at 500°C however lead to a decrease in the PL intensity. Cho *et al*. [8] noted the same effect during the investigation of optical properties of sol-gel derived $Y_2O_3:Eu^{3+}$ thin film phosphors for display applications.

Conclusion

Thin films of the $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ phosphor powder were successfully prepared at different substrate temperatures using the PLD technique. XRD showed that the crystallinity of the films has improved with an increasing substrate temperature up to 300°C. The crystallinity was affected by interdiffusion at 500°C. The films deposited at 300°C also showed the highest PL intensity. AFM images showed nano-meter sized grains and at a 22°C substrate temperature there was a mixture of small grains and large grains. As the substrate temperature was increased to 300°C larger and more uniform grains formed that increased the surface roughness. At 500°C, a decrease in the surface roughness was, however, observed. The results indicate that a substrate temperature of 300°C in an O_2 atmosphere provides good conditions to grow films with high PL intensity and good morphological characteristics.

Acknowledgments

Gratitude to Brian Yalisi and Dr Lorinda Wu at the NLC, CSIR in Pretoria for assisting with the film growth using the PLD technique. Dr Coetsee-Hugo for NanoSAM measurements. This work is based on the research supported by the South African Research Chairs Initiative of the Department of Science and Technology and the National Research Foundation of South Africa. The University of the Free State is acknowledged for financial support.

References

[1] Bae J S, Shim K S, Kim S B, Jeong J H, Yi S S and Park J C 2004 *J. Cryst. Growth* **264** 290

[2] Christoulakis S, Suchea M, Katsarakis N and Koudoumas E 2007 *Appl. Surf. Sci.* **253** 8169.

[3] Fan X M, Lian J S, Guo Z X and Lu H J 2005 *Appl. Surf. Sci.* **239** 176.

[4] Eason R (Editor), Pulsed laser deposition of thin films application-led growth of functional materials, Wiley Interscience, 2006.

[5] http://www.phosphoo-technology.com/products/ctr.htm [Accessed 29 May 2012]

[6] Dlamini S T S, Swart H C and Ntwaeaborwa O M 2013 *Sol. State Sci.* 10.1016/j.solidsate-sciences.2013.06.009

[7] Wu J L, Gundiah G and Cheetham A K 2007 *Chem. Phys. Lett.* **441** 250

[8**]** Cho J Y, Ko K and Do Y R 2007 *Thin Solid Films* **515** 3373.

[9] Hua R, Lei B, Xie D and Shi C 2003 *J. Solid State Chem.* **175** 284

[10] Obrien T A, Rack P D, Holloway P H and Zerner M C 1998 *J. Lumin.* **78** 245

[11] Coetsee E, Swart H C and Terblans J J 2007 *J. Vac. Sci. Technol. A* **25** 4