Luminescence of $Y_2SiO_5$:Ce Nanocrystalline Thin Films

E. Coetsie, J. J. Terblans, and H.C. Swart
Department of Physics, University of the Free State,
P. O. Box 339 Bloemfontein, ZA9300, South Africa

J.M. Fitz-Gerald
Department of Materials Science & Engineering, University of Virginia,
395 McCormick Road, Charlottesville, VA 22904-4745, U.S.A.

J. R. Botha
Department of Physics, Nelson Mandela Metropolitan Universiteit,
P. O. Box 77000, Port Elizabeth, 6001, South Africa
(Received 22 May 2008; Accepted 20 October 2008; Published 4 April 2009)

The luminescent properties of cerium doped yttrium silicate ($Y_2SiO_5$:Ce) nanocrystalline thin films that were grown during the systematic investigation of process parameters for pulsed laser deposition (PLD) (KrF laser, 248 nm on a silicon (Si)(100) substrate), were studied. Parameters such as ambient pressure (vacuum ($5 \times 10^{-6}$ Torr), $1 \times 10^{-4}$ Torr and 1 Torr O$_2$ pressure), laser fluences ($1.6 \pm 0.1$ J·cm$^{-2}$ and $3.0 \pm 0.3$ J·cm$^{-2}$) and substrate temperatures (400 and 600°C) were varied and the results are compared. The surface morphology was monitored by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and atomic force microscopy (AFM). The monoclinic X$_1$ crystal structures of the $Y_2SiO_5$:Ce films were studied with x-ray diffraction (XRD). The O$_2$ ambient pressure of 1 Torr resulted in the growth of a thin film consisting of spherically shaped nanoparticles and the thin film grown in vacuum resulted in a uniform thin film. The cathodoluminescence (CL) and photoluminescence (PL) intensity of the nanofilm is considerably higher than the uniform layer. The higher fluence resulted in a thicker thin film with a more compact agglomerated particle distribution. The lower fluence leads to a higher density distribution of smaller nanoparticles. The increase in substrate temperature to 600°C also resulted in a higher PL intensity. CL scanning images (with two different PMT voltages (650 and 850 eV)) were obtained on some of the thin films during SEM measurements. Emission from the thin films seems to occur from luminescent centres in the micron particles as well as from smaller particles around the bigger micron particles with the higher PMT voltage. [DOI: 10.1380/ejssnt.2009.369]

Keywords: $Y_2SiO_5$:Ce; Nano-particles; Semiconductor thin film structure; Photoluminescence; Cathodoluminescence

I. INTRODUCTION

The latest phosphor research delivered promising results for several new applications. Different phosphors with different dopants and thus different colours and luminescent properties are investigated. The investigations are mainly focussed on the preparation methods (such as sol-gel synthesis and pulsed laser deposition (PLD)) of phosphor powders as well as thin films, on the degradation, enhancing the luminescence, long afterglow as well as on nanophosphors. Each investigation creates opportunities for new phosphor research fields and thus improvement.

The main purpose of this study is to improve the luminescent efficiency of the phosphors used in field emission displays (FEDs) [1, 2]. PLD is a well known fast and effective technique to grow thin films for possible application in high performance electronic and optical devices (e.g. FEDs). Thin film phosphors have some advantages over powders in the FED environment, such as a reduction of light scattering and a good thermal contact between the screen and the faceplate [3, 4] but the intensity is still a great problem.

Particle formation is, however, a major drawback of PLD and it usually is the main limiting factor in the application field. These high performance electronic and optical devices require particle free films. The formation and emission of the particles strongly depend on the type of material used as the target and it is based on various physical phenomena such as the dislodgement of uniformities protruding from the target surface, gas phase clustering of the evaporated material due to supersaturation (in high gas pressures) and the generation of liquid phase droplets. Particles can therefore be in the vapour, liquid or solid phase [5, 6].

One of the solutions to the particle formation problem is optimization of the laser process parameters such as the ambient pressure (oxygen), laser spot size, laser pulse frequency, number of pulses and the substrate temperature. Surface morphology and thickness can be controlled by varying of the growth parameters [4, 5].

$Y_2SiO_5$:Ce, is a blue emitting (double shoulder peak between 400 and 500 nm) rare earth phosphor. Light emission in rare earth phosphors is due to characteristic luminescence in the atom itself. In this paper $Y_2SiO_5$:Ce nano- and uniform thin films were grown with PLD. The ambient pressure, laser pulse fluence and the temperature were varied during the growth process. The surface morphology and luminescent properties are compared.

*This paper was presented at the 14th International Conference on Solid Films and Surfaces (ICSFS-14), Trinity College Dublin, Ireland, 29 June - 4 July, 2008.
†Corresponding author: swarthc.sci@ufs.ac.za
II. EXPERIMENTAL SETUP

Silicon (Si) (100) substrates were cleaned in acetone for 5 min, in an ultrasonic water bath and then for another 5 min in methanol. The substrates were blown dry with nitrogen (N₂) gas. Commercially available Y₂SiO₅:Ce standard phosphor powders from Phosphor Technology (UK) were pressed into a pellet and annealed at 600°C for 24 h in vacuum to remove any water vapour that might be present in the powder. The Lambda Physik 248 nm KrF excimer laser was used to ablate the thin films on the substrates. A laser energy of 250 mJ per pulse, a repetition rate of 8 Hz and two different pulse fluences were used to ablate the thin films. The vacuum base pressure was 5×10⁻⁶ Torr before the system was backfilled with O₂ gas to two different pressures, 1×10⁻² Torr and 1 Torr. Two substrate temperatures were used, 400 and 600°C and the target to substrate distance was 4 cm. Other thin films were grown with different parameters, in a previous research study, and were used in this study for CL scanning. These thin films were prepared with PLD but with a XeCl laser (λ = 308 nm), 81.8±0.2 mJ energy per pulse, pulse frequency of 10 Hz in 7×10⁻³ Torr O₂ and a substrate temperature of 400°C with a target to substrate distance of 3.5 cm. Some of the Y₂SiO₅:Ce thin film (ablated with 6600 pulses) was coated with tin oxide (1200 pulses). Surface morphology and structure were monitored with scanning electron microscopy (SEM) backscattering electron spectroscopy (BSE), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and X-ray spectroscopy (XRD). SEM, BSE and EDS results were done with a Shimadzu Superscan SSX-550 system and the data were collected with an Ocean Optics S2000 spectrometer. PL measurements were done with a HeCd laser and a Varian Cary Eclips fluorescent spectrophotometer equipped with a xenon flash lamp (λ = 325 nm). CL scanning images were done during SEM measurements with a Mono-CL 3 system from Gatan.

III. RESULTS AND DISCUSSION

A. SEM/BSE and EDS

Figure 1 shows the SEM images of the two thin films that were ablated in a 1 Torr O₂ ambient with a fluence of (a) 3.0±0.3 J·cm⁻² and (b) 1.6±0.1 J·cm⁻². The SEM images indicate nano-particulate features on the surfaces with a few bigger micron size particles. From the SEM images it is clear that the sizes of the particles formed at the lower fluence are smaller than the particles that were ablated with the higher fluence and also less agglomerated. The particle sizes of the higher fluence vary mainly between 130 to 140 nm (and bigger) and the lower fluence sizes vary between 50 and 60 nm. The higher fluence particles consist of smaller particle ranging from 5 to 30 nm as measured with AFM. The thin films that were ablated with the same fluences in vacuum and in 1×10⁻² Torr showed a uniform layer (results not shown here) with bigger micron size particles on the surface. These bigger micron size particles on the surface may create problems in electronic devices. BSE images, Fig. 2, were used to obtain the positions at which EDS analysis were made on films a) ablated in 1 Torr O₂ and b) in vacuum at 600°C. (BSE images were done with a 15 keV beam energy, magnification of ×40,000 and a scale of 500 nm.)

![Figure 1: SEM images of the two thin films ablated in a 1 Torr O₂ ambient at 600°C with a fluence of a) 3.0±0.3 J·cm⁻² and b) 1.6±0.1 J·cm⁻² (5 kV beam energy, magnification of ×40,000 and a scale of 500 nm).](image1)

![Figure 2: BSE images and EDS analysis of the thin films ablated with a fluence of 3.0±0.3 J·cm⁻² in a) 1 Torr O₂ and in b) vacuum at 600°C. (BSE images were done with a 15 keV beam energy, magnification of ×40,000 and a scale of 500 nm.)](image2)

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
bient, high fluence \((3.0 \pm 0.3 \text{ J-cm}^{-2})\). The surface structure is less compact (lesser agglomeration of particles than the \(600^\circ\text{C}\), Fig. 1(a))—A rough estimate of the number of particles/cm\(^2\) for the 400 and the \(600^\circ\text{C}\) samples is \(3 \times 10^9\) particles/cm\(^2\) compared to \(4 \times 10^9\) particles/cm\(^2\). These bigger particles are however an agglomeration of smaller particles. The value for the lower fluence, Fig. 1(b) is in the order of \(15 \times 10^9\) particles/cm\(^2\).

**B. AFM**

Figure 4 shows the AFM images that were obtained in contact mode on the thin films ablated in 1 Torr and in vacuum with the two laser fluences and the substrate temperature at \(600^\circ\text{C}\). The nano-particles are clearly visible for the 1 Torr O\(_2\) ablated samples a) higher fluence and c) lower fluence. The height z-range values, 119 nm for a), 187 nm for b), 53 nm for c) and 78 nm for d), show a thicker layer of nanoparticles for the higher laser fluence. These nanoparticles result in a very rough surface compared to the thin films ablated in vacuum. The rougher surface results in better CL and PL intensities. Deposition in \(1 \times 10^{-2}\) Torr showed uniform thin films (results not shown here). Uniform films ablated in vacuum at the two different fluences b) higher and d) lower have thicknesses of 187 and 78 nm, respectively, as measured at the interfaces of the regions not covered by the ablated thin film and the thin film. The higher fluence led to a thicker uniform thin film as expected.

**Particle formation:**

The mean free path of the particles in a low ambient pressure is longer compared to the mean free path at higher ambient pressures. More collisions between the ultrafine particles (vaporised particles close to the target) at a higher ambient pressure lead to nucleation and growth into bigger nano particles before arrival at the substrate. In vacuum there are virtually no collisions between the particles before reaching the substrate. Longer residence time of the particles in the plume, as is the case at higher ambient pressures, lead to bigger evenly distributed particles [5]. See schematic presentation in Fig. 5 [7].

**C. XRD**

The powder used as a target has a monoclinic crystal structure of Y\(_2\)SiO\(_5\):Ce X\(_1\) -phase with space group P2\(_1\)/c [8]. The XRD results for the thin films showed low intensity peaks for (402) and (013) that were in agreement with the X\(_1\) phase. The peaks were most pronounced for the \(600^\circ\text{C}\) high fluence samples. Sun et al. [1] studied silicate phosphor (Y\(_2\)SiO\(_5\):Ce, Zn\(_{2}\)SiO\(_4\):Mn and CaSiO\(_3\):MnPb) thin films prepared by PLD. The substrate temperature used was \(300^\circ\text{C}\) (as grown) and the thin films were annealed for 5 hr in air, at 800 and then 1000°C. The XRD results for the Y\(_2\)SiO\(_5\):Ce thin films showed an increase in crystallinity with an increase in annealing temperature with the two main peaks for the X\(_1\)-phase only visible after annealing at 1000°C, (402) and (013). A PL intensity increase was clearly observed for the higher annealing temperature. The enhanced luminescence was attributed to the increased crystallinity as well as the rougher surface morphology [8].
D. CL and PL

CL and PL were also done on the nano- and uniform thin films that were grown at the different process parameters. The effect of the rougher surface (nano- versus uniform), the small increase in O$_2$ ambient, the high and low fluence and the increase in substrate temperature from 400 to 600°C on the luminescent intensity were analysed. Figure 6(a) shows the more intense CL intensity of the nano- thin film (1 Torr O$_2$) and the digital images of the blue light from (b) the uniform and (c) the nano- thin film. The higher CL intensity of the nano- thin film is a result of more photons exiting the spherically shaped nano particles in comparison with the uniform thin layer were the photons get totally internally reflected (routher surface). This was also reported by Coetsee et al. [3] during the investigation of the CL intensity degradation of tin oxide coated Y$_2$SiO$_5$:Ce thin films grown by PLD. A rougher surface would thus result in better luminescence intensity compared to a uniform surface.

During the PLD process the growth of the thin films resulted in Ce$^{3+}$ occupying different lattice sites in the complex crystal structure of the Y$_2$SiO$_5$ host. The broad band spectra, observed in Figs. 6, 7 and 8 is a contribution of the two different sites of the Ce$^{3+}$ ion in the host matrix and the difference in orientation of the neighbour ions in the crystal [9–12]. The luminescent mechanism is however much more complicated and will be reported in more detail later. Figure 7 shows the increase in PL intensity when the O$_2$ pressure was increased from vacuum to $1 \times 10^{-2}$ Torr and to 1 Torr (high fluence, 600°C). The increase in the ambient pressure leads to the formation of the nano-particles (see particle formation in section 3.2) and thus an increase in the luminescent intensity. The size and growth of the particles are indeed controlled by the residence time of the particles in the plume when an ambient gas is used. The same result was found for the low fluence but further research need to be done with a more variety of gas pressures.

Figures 8(a) and (b) show the increased PL intensity of the thin film ablated with the higher fluence and higher substrate temperature. If the laser power is kept constant and the laser spot size is focussed more tightly, the fluence will increase and this will also increase the particle number density [5]. As mentioned earlier the higher fluence ablated a better crystalline, a thicker and denser thin layer and this result in the increased luminescent intensity. As no significant difference in particle sizes (only more agglomeration of the particles) could be seen from the SEM images for the increase in temperature, it is known that higher temperature result in better luminescent intensity due to the rougher surface formed [1, 5].

E. CL scanning

Interesting to note was the CL scanning image of a bigger particle on the surface of the thin film that was ablated with PLD in a 1 Torr O$_2$ ambient (600°C, low fluence). The thin film consists of nano-Y$_2$SiO$_5$:Ce particles with

---

FIG. 5: Schematic diagram to illustrate the agglomeration of the particles in the plume in a higher ambient pressure (1 Torr O$_2$) before reaching the substrate [7].

FIG. 6: (a) CL intensity and digital images of the blue light from (b) the uniform and (c) the nano- thin film, low fluence and 600°C.

FIG. 7: PL spectra of the thin films ablated at different O$_2$ ambient, with the high fluence and a substrate temperature of 600°C.

FIG. 8: PL spectra for the high and low fluence (600°C) for (a) the thin films ablated in vacuum and in 1 Torr O$_2$ and (b) substrate temperature of 400 and 600°C (high fluence).
FIG. 9: (a) SEM image and (b), (c) CL images of the Y$_2$SiO$_5$:Ce thin film (1 Torr, low fluence, 600°C) performed at 15 kV electron beam energy, magnification of ×10,000 and a scale of 1 µm with a photomultiplier tube (PMT) voltages of 650 and 850 V, respectively.

FIG. 10: CL images of (a) the uncoated Y$_2$SiO$_5$:Ce and (b) a 60 nm tin oxide coated thin films performed at 15 kV electron beam energy, magnification of ×1,000 and ×1,500 respectively, a scale of 10 µm with a photomultiplier tube (PMT) voltage of 650 V.

bigger micron size particles on the substrate as can also be seen from Fig. 1(b). The CL scanning images that were obtained during SEM measurements Fig. 9(b), at a PMT voltage of 650 eV, indicated emission from 3 small light emitting centres inside the bigger micron particle. These centres are not clearly defined in the SEM image, Fig. 9(a). In Fig. 9(c) the PMT voltage was increased to 850 V and the effect of a higher luminescence is clearly visible. Emission seems to occur from the whole micron particle as well as from the smaller particles around the particle. The smaller particles did not show effective emission with the lower PMT voltage, Fig. 9(b).

Cathodoluminescence that was done on the nano-thin films resulted in a higher CL intensity than the uniform thin film [8]. The reason for this is due to a lesser effect of total internal reflection for the photons exiting the spherical micron and nano-particles. More photons get reflected internally in the uniform thin film than in the spherically shaped particles. Due to the high intensity of the light coming from the bigger particles it seems that light is only coming from the bigger particles but as seen in Fig. 6 (c) the total layer is luminescent. Thin films were also prepared with PLD with a XeCl laser (λ = 308 nm), 81.8±0.2 mJ energy per pulse, pulse frequency of 10 Hz in 7.5×10$^{-3}$ Torr O$_2$ and a substrate temperature of 400°C.

The one Y$_2$SiO$_5$:Ce thin film (ablated with 6600 pulses) was coated with a 60 nm tin oxide layer (1200 pulses). The layer was coated in order to investigate the effect of an extra transparent coated layer, on the degradation of the phosphor and the luminescent intensity. The coated layer succeeded in preventing degradation but it absorbs the photons and thus reduces the luminescent intensity [8]. Energy of the electrons used for the excitation is also absorbed by the protected thin film and will also resulted into a lower intensity [13]. Figure 10 shows the CL scan results of the (a) uncoated and (b) tin oxide coated thin films. There is a definite increase in luminescent intensity with the uncoated thin film which indicates the photon absorption effect of the extra tin oxide coated layer. CL intensity is mainly coming from the bigger spherical particles on the surface as seen from these images. The bigger agglomerated particles formed at the higher temperature and higher fluence were much more efficient in light output, as seen from the previous section.

IV. CONCLUSION

Y$_2$SiO$_5$:Ce uniform thin films were successfully grown with PLD onto a Si (100) substrate in a vacuum pressure of 5×10$^{-6}$ Torr and nano-particle thin films were grown in a 1 Torr O$_2$ ambient. The nano-thin films lead to an increase in PL and CL intensity. The higher fluence resulted in a thicker thin film with a more compact agglomerated particle distribution. The lower fluence lead to a higher density distribution of smaller nanoparticles. Thin films grown with a higher fluence resulted in a thicker uniform layer for the thin films grown in vacuum. The thin films grown with the higher fluence resulted in better crystallinity and better luminescent intensities. The increase in substrate temperature from 400 to 600°C also resulted in an increased luminescence due to a rougher surface that
formed. For better luminescent intensity the thin films should have a rougher surface (spherically shaped particles achieved via increased substrate temperature and increased ambient pressure).

**Acknowledgments**

The authors would like to acknowledge Phosphor Technology LTD for supplying the phosphor samples, the NLC at the CSIR Pretoria for the use of the laser facilities, the South African National Research Foundation (NRF) and National Metrology Institute of South Africa (NMISA) for financial assistance, and Prof. P. W. J. van Wyk from the Centre of Confocal and Electron Microscopy for SEM, BSE and EDS measurements. One of the authors (JRB) acknowledges that this work is based upon research supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation.