Optical properties of $SrGa_2S_4:Ce^{3+}$ thin films prepared by pulsed reactive cross laser ablation (PRCLA) technique

P A Moleme, H C Swart and O M Ntwaeaborwa[1]

Department of Physics, University of the Free State, P O Box 339, Bloemfontein ZA 9300, South Africa.

e-mail: ntwaeab@ufs.ac.za or molemepa@ufs.ac.za

Abstract. $SrGa_2S_4:Ce^{3+}$ thin films were prepared by the pulsed reactive cross laser ablation (PRCLA) technique. Characterization of the films was carried out with scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). Cathodoluminescence (CL) and photoluminescence (PL) properties of the films were investigated. The films were prepared using different substrate temperatures, number of pulses and working pressures. A highly crystalline $SrGa_2S_4$ layer was observed when the substrate temperature of 400°C was used. The XRD patterns showed that the growth of the films was sensitive to substrate temperature. PL and CL showed one broad band that can be fitted with two Gaussian peaks according to the two Ce^{3+} radiative transitions at lower substrate temperatures, low and high pulses and in O_2 atmosphere. At high substrate temperature and in Ar atmosphere, the emission peaks were red-shifted to resemble Ce^{3+} emission in a SrS host for both UV and high energy electrons excitation. The AFM images before annealing exhibited a smooth surface at a low substrate temperature, which became rougher at high substrate temperatures and after annealing in vacuum at a temperature of 700°C. Non-uniformity in particles of the films and smooth surfaces were observed from the SEM images.

1. Introduction

Thin films of $SrGa_2S_4:Ce^{3+}$phosphor are promising candidates for full colour electroluminescence (EL) and field emission displays (FED) because of the phosphor's good optical properties [1]. These films were previously prepared using different techniques such as Rutherford sputtering (RF), molecular beam epitaxy (MBE), reactive multi-source deposition (MSD), deposition from binary depositions (DVB), reactive multisource deposition, flash evaporation method, metal-organic chemical vapour deposition (MOCVD), two target pulse pulsed-electron-beam evaporation (EBE) and Pulsed Laser Deposition (PLD) techniques [2], [3]. In this study the films were prepared using the pulsed reactive cross laser ablation (PRCLA) technique in which the gas pulse crosses the laser plume. The structure, morphology, topography and luminescent (photoluminescence and cathdoluminescent) properties of the films were investigated.

2. Experimental details

Silicon (Si) (100) substrates were first cleaned with KIMTECH SCIENCE KIMWIPES obtained from Kimberly Clark Professionals. A pellet with a 2.4 cm diameter and 6 mm thickness was prepared by pressing the $SrGa_2S_4:Ce^{3+}$ powder for 1 hour at a pressure of 1.96 x 10^7 mbar. The pellet was then annealed for 6 hours at 600°C in vacuum to improve its hardness. It was then mounted on a rotating holder lying diagonally to a heater on which Si substrates were mounted. The distance between the target and the substrates was maintained at 4 cm during the deposition of each film. The Lambda Physik EMG 203 MSC 308 nm XeCl excimer laser was used to ablate the target. The films growth

---

[1] Corresponding author: ntwaeab@ufs.ac.za

was carried out in a chamber which was first evacuated to a base pressure of 8 x 10^{-5} mbar before backfilling to pressures of 1.0 x 10^{-2} mbar Ar and 1.0 x 10^{-2} mbar O_2, where Ar and O_2 were used as pulse gases. The films were deposited at different substrate temperatures ranging from 400°C to 600°C using 28 800 and 57 600 pulses. The laser beam was operated at an 8 Hz repetitive rate. The substrate temperature, number of pulses and the working pressure were varied during the deposition of the thin phosphor films. Characterization of the films was carried out with scanning electron microscope (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). Cathodoluminescent (CL) and photoluminescent (PL) spectra were recorded with a S2000 Ocean Optics spectrometer and Varian Cary Eclipse fluorescence spectrophotometer respectively. Auger electron spectroscopy (AES) was used to analyze the elemental (chemical) composition of the films.

3. Results and discussions

Shown in figure 1 are the XRD patterns and the Miller indices of the $SrGa_2S_4:Ce^{3+}$ films prepared at different substrate temperatures ranging from 400 to 600°C. A highly crystalline $SrGa_2S_4$ layer was observed at the growth temperature of 400°C with 28 800 pulses in an Ar environment. From the comparison with the standard powder pattern of $SrGa_2S_4$ (JCPDS file no. 77-1189) all the peaks, except an identified impurity peak (marked x) at $2\theta = \sim 47^{o}$, in figure 1 (a) were found to belong to the orthorhombic $SrGa_2S_4$ crystal structure. The (10 4 4) diffraction peak is more intense than that observed from $SrGa_2S_4:Ce^{3+}$ powder reported elsewhere [4].

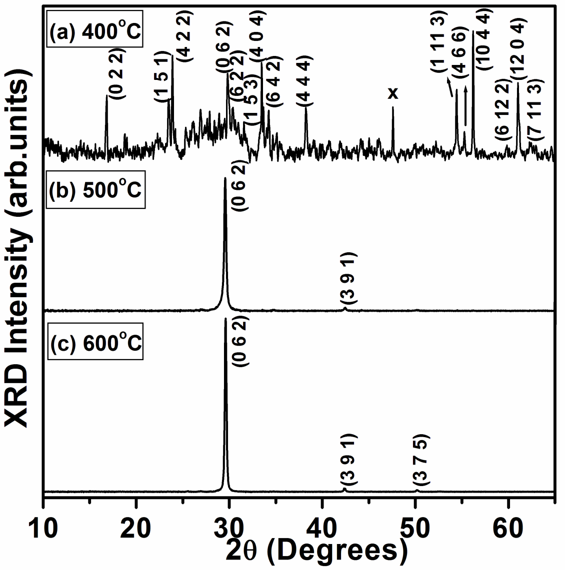

Figure 1. The diffraction patterns of the $SrGa_2S_4:Ce^{3+}$ films deposited at different substrate temperatures.

A preferential growth along the orientation (0 6 2) was observed when the substrate temperature was increased to 500°C and 600°C. In addition, small signatures of the (3 9 1) and (3 7 5) peaks which also belong to the orthorhombic $SrGa_2S_4$ crystal structure were detected. Similar results as the once observed at 400°C and 500°C substrate temperatures were reported by Heikkinen et al [5]. The XRD patterns in figure 1 show that the film growth is sensitive to the substrate temperature. The intensity of the (0 6 2) peak was observed to increase with an increase in the substrate temperature from $T_{substrate}$ = 400°C to 600°C. These results also indicate that crystallinity can be achieved even without post-deposition annealing. Tanaka et al [6] investigated the crystallinity of the $SrGa_2S_4:Ce^{3+}$ thin films grown on quarts glass substrates with the MBE technique. The films were grown at substrate temperatures of 400°C to 600°C. They reported a gradual decrease in the XRD peak intensity at $T_{substrate} > 600°C$ and $T_{substrate} < 500°C$ and found the best substrate temperature for $SrGa_2S_4$ film growth to be around 560°C. Yang et al [7] reported the same substrate temperature as the best for $SrGa_2S_4$ films growth. The XRD patterns for the films deposited at different number of pulses and in O_2 environment exhibited poor crystallinity.

For the range of all deposition conditions investigated, the SEM images of all films exhibited small and big spherical particles distributed unevenly on the smooth surfaces of the films. Auger survey was performed on the films and the major elements, namely, Sr, Ga, and S were detected from all the films. In addition, atmospheric O and C were also detected. Shown in figure 2 (a) is the SEM image of the surface of the $SrGa_2S_4:Ce^{3+}$ film deposited at 400°C and in figure 2 (b) is the Auger survey spectrum for the film.

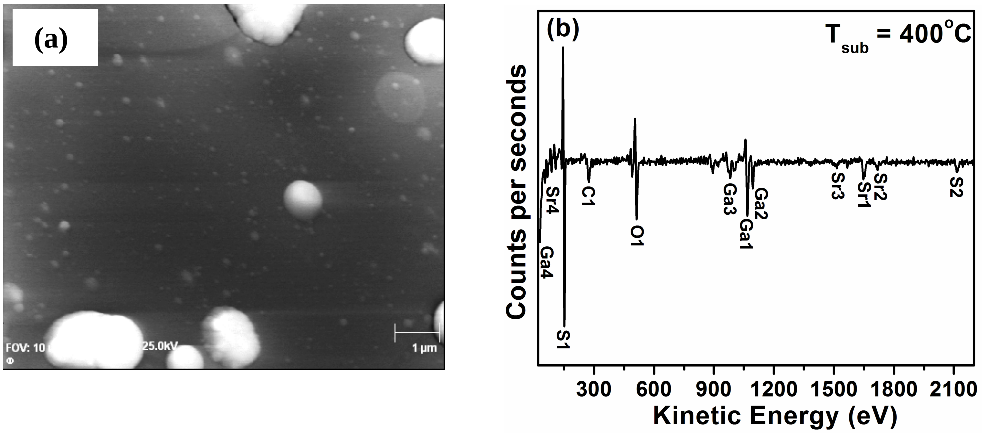

Figure 2 (a) The SEM micrograph and **(b)** Auger survey spectrum of the $SrGa_2S_4:Ce^{3+}$ films deposited at 400°C.

Figure 3 (a) – (c) and (d) – (e) show respectively the AFM images of the films deposited at the substrate temperatures of 400, 500, and 600°C before and after annealing at 700°C in vacuum.

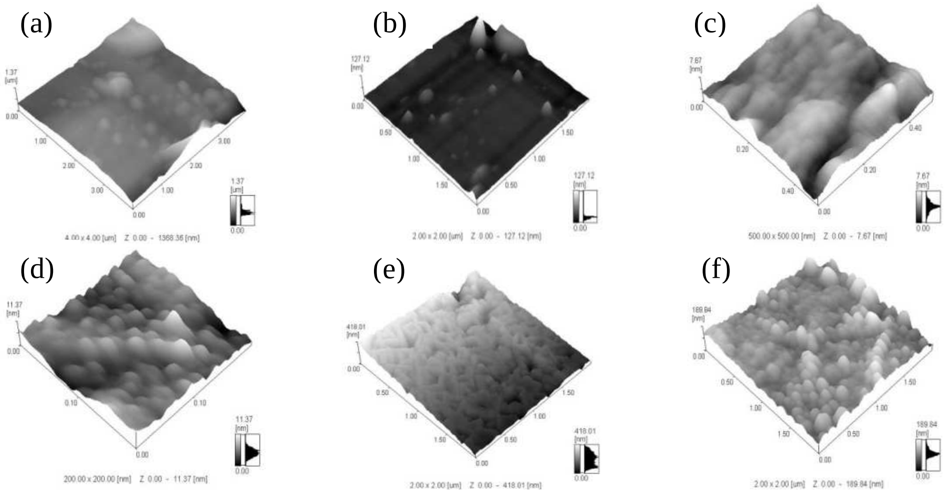

Figure 3. AFM images for the un-annealed $SrGa_2S_4:Ce^{3+}$ films prepared at **(a)** 400°C, **(b)** 500°C, **(c)** 600°C. Images **(d), (e)** and **(f)** show, respectively, the films annealed in vacuum at 700°C.

At 400°C (figure 3 (a)), the film was smooth with uneven distribution of few spherical particles of different sizes on the surface. After annealing (figure 3 (d)) the surface became rough with an increased number of spherical particles on the surface. The smooth surface with steps was observed at 500°C as depicted in figure 3 (b), with few non-uniform cylindrical particles of different sizes. Annealing the film (figure 3 (e)) resulted in fairly rough surface covered completely with nano-rods like particles. The surface became rough at 600°C (figure 3 (c)), with big particles and after annealing (figure 3 (f)) the roughness and the number of cylindrical particles on the surface layer increased. Root mean square (rms) values of the unannealed films were measured by AFM. For the film prepared at 400°C with 57 600 number of pulses, the rms value was 16.5 nm while that of the film deposited with 28 800 pulses was 35nm. It is therefore clear that the surface roughness decreased with increasing number of pulses. This was ascribed to the increase in the thickness of the film's layer as number of pulses were increased, thus improving the film's homogeneity and planarity [8].

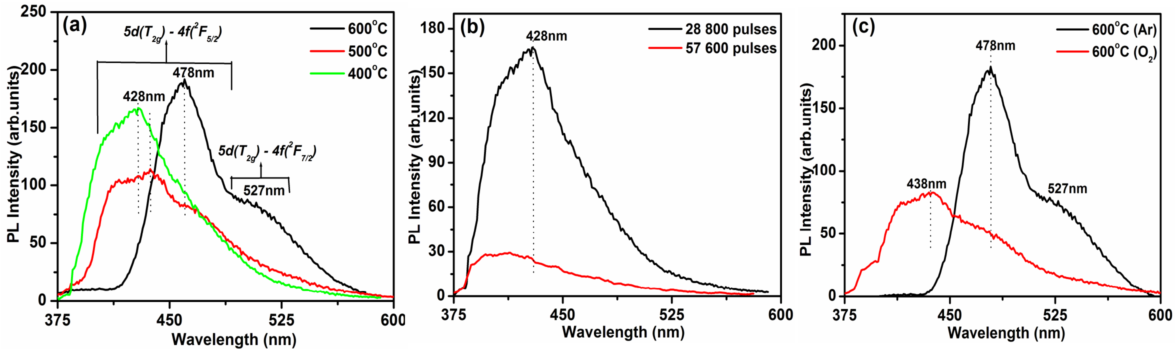

Figure 4. PL spectra of the $SrGa_2S_4$:Ce^{3+} films prepared at **(a)** different substrate temperatures, **(b)** different number of pulses, and **(c)** in Ar and O_2 atmospheres.

Shown in figure 4 (a-c) are the PL emission spectra for the films deposited at different substrate temperatures, number of pulses and cross pulse gases (Ar and O_2) respectively. At 400°C, one broad band that can be fitted with two Gaussian peaks according to the two Ce^{3+} emission peaks which are known to originate from 5d (T_{2g}) → 4f ($^2F_{5/2}$) and from 5d (T_{2g}) → 4f ($^2F_{7/2}$) radiative transitions of Ce^{3+} were observed and were similar to the data published elsewhere [9]. As the substrate temperature was increase to 500°C, a broad band with a small shoulder at approximately 485 nm was observed and a slight shift of the emission peak to the right as indicated in the figure. In addition, the film deposited with 28 800 pulses was more intense than that deposited with 57 600 pulses (figure 4 (b)) as expected from a thicker layer obtained from the increase in the number of pulses. A further shift to the right was observed for the film deposited at the 600°C substrate temperature in the Ar atmosphere. The resulting spectrum resembles the Ce^{3+} emission in a SrS host [10]. While the possible phases relating to SrS were not detected in the XRD data, the X-ray photoelectron spectroscopy data in ref [4] confirmed that SrS was formed. Note that the well known two emission peaks associated with the crystal field splitting of the Ce^{3+} were clearly resolved and were observed at 478 and 527 nm for the film deposited at the substrate temperature of 600°C. Similar results were reported elsewhere [11], [12]. Generally, the red-shifting of the emission peaks was simultaneous with increasing substrate temperature. The less PL emission in figure 4 (c) for the film deposited in the O_2 environment was ascribed to the possibility of a chemical reaction of strontium with highly reactive oxygen to form a non-luminescent SrO layer, thus affecting the stoichiometry near the interface and causing a reduction in the PL intensity. Depicted in figure 5 are the CL emission spectra exhibiting the well known two emission peaks of the Ce^{3+} for the $SrGa_2S_4$: Ce^{3+} films deposited at different parameters. At 400°C, the film showed the same pattern as the CL emission of the powder phosphor reported in ref [2]. That is, the two well known emission peaks associated with 5d (T_{2g}) → 4f ($^2F_{5/2}$) and from 5d (T_{2g}) → 4f ($^2F_{7/2}$) radiative transitions of Ce^{3+} were observed at 443 and 585 nm.

Again there was a red-shift of the emission peaks with increasing substrate temperature. Consistent with the PL data, the highest CL intensity was observed from the film deposited with 28 800 pulses as shown in figure 5 (b). It was again noticed that the film deposited in Ar atmosphere at 600°C was more intense than that deposited in O_2 atmosphere as shown in figure 5 (c). The inset of figure 3(c) is the stand alone spectrum of the film deposited in O_2 showing that the emission spectrum resemble those of the film deposited at a 400°C (figure 1(a)) and different number of pulses (figure 2).

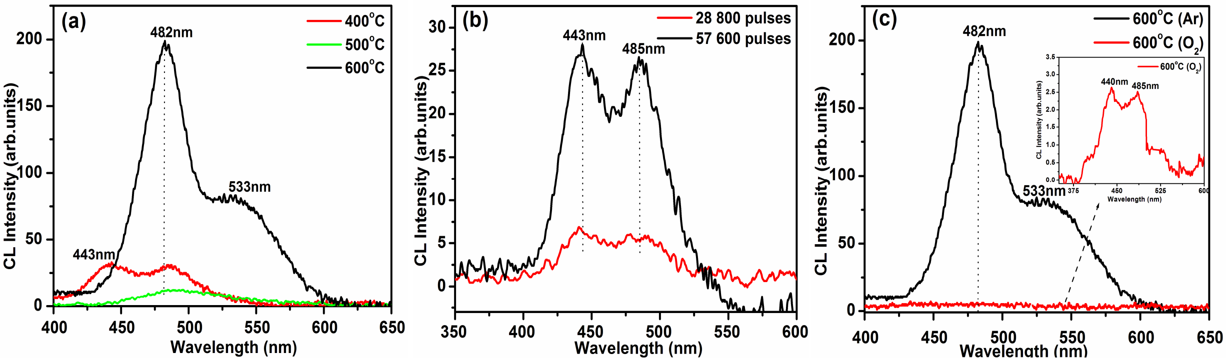

Figure 5. CL emission spectra of the $SrGa_2S_4:Ce^{3+}$ films deposited at **(a)** various substrate temperature, **(b)** different number of pulses and **(c)** in Ar and O_2 atmosphere.

4. Conclusion

$SrGa_2S_4:Ce^{3+}$ films were prepared successfully for the first time by the PRCLA technique. The growth temperature of 400°C showed a highly crystalline $SrGa_2S_4$ layer and also CL emission pattern similar to the one of the $SrGa_2S_4:Ce^{3+}$ powder was attained at this substrate temperature. At higher substrate temperatures, a shift to SrS emission occurred for both PL and CL emission peaks. Non-uniformity in particles (big and small) of the films and smooth surface were observed from SEM images. The AFM images showed smooth surface before annealing at low substrate temperature and at high substrate temperature the films surface became more rough as well as after annealing in vacuum at 700°C temperature.

References

[1] Nakanishi Y, Uekura N, Nakano F and Hatanaka Y 1997 *J. of Lumin.* **72-74** 373-374
[2] Gambarov E F and Bayramov A, Academy of Sci. of Azerbaijan, Institute of Physics.
[3] Bènalloul P, Barthou C and Benoit J 1998 *J. Alloy Compd.* **275-277** 709-715
[4] Moleme PA, Swart HC and Ntwaeaborwa O M 2011 MSc Dissertation, University of the Free State, South Africa
[5] Heikkinen H, Johansson L-S, Nykänen E and Niinistö L 1998 *Appl. Surface Sci.* **133** 205-212
[6] Tanaka K, Inoue Y, Okamoto S and Kobayashi K 1995 *J. of Crystal Growth* **150** 1211-1214
[7] Yang T, Wagner B, Chaichimansour M, Park W, Wang Z, and Summers C 1996 *J. Vac. Sci. Technol.* B **14** 3
[8] Christoulakis S, Suchea M, Katsarakis N and Koudoumas E 2007 *Appl. Surf. Sci.* **253** 8169-8173
[9] Mhlongo G H, Ntwaeaborwa O M, Dhlamini M S and Hillie K T 2011 *J. Alloy Compd.* **509** 2986 - 2992
[10] Kumar V, Pitale S S, Biggs M-M, Nagpure I M, Ntwaeaborwa O M and Swart H C 2010 *Mater. Lett.* **64** 752 - 754
[11] Chunxiang X, Zhidong L, Zheng X and Xurong X 1998 *Chinese Sci. Bull.* **43** 7 603-605
[12] Chunxiang X, Zheng X, Xurong X and Zhidong L 1999 *Solid State Comm.* **109** 183-187