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Characterization of Laser Ablated $SrAl_2O_4:Eu^{2+}$, Dy^{3+} Thin Films Deposited on the Optimum Substrate Temperature Range

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Abstract: The morphological, structural and photoluminescence (PL) of laser ablated $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited on optimum substrate temperature range of 200-500°C are reported. The 200-500°C substrate temperature was considered, since on that range, low cost highly emitting $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films are always produced. The surface morphology analysis of the films was done by using the scanning electron microscopy (SEM) and atomic force microscopy (AFM). The energy dispersive X-ray spectrometer (EDS) was employed for elemental composition analysis. The structural analysis was done by the X-ray diffraction (XRD) technique. The photoluminescence (PL) data collection was done by using Cary Eclipse fluorescence spectrophotometry. The films were excited by the UV light from the xenon lamp. The highest green emission intensity with a peak at 517 nm and highest initial afterglow intensity were recorded by the sample that was deposited at 350°C. The green peak at 517 nm is attributed to $4f^65d^1 \rightarrow 4f^7$ Eu^{2+} transitions. AFM images with well defined grains were observed on the films deposited at temperatures higher than 200°C. The EDS elemental composition analysis showed that the films consist of all the main elements of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, i.e., Al, Sr, O. The changes in the film photoluminescence and morphology with the substrate temperature are discussed.

Keywords: $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, SEM, AFM, Thin Film, Substrate Temperature, PL

1. Introduction

Over the last few years, significant research on the growth and characterization of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} luminescent thin films has been conducted and published [1-5]. $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films have attracted a lot of attention since they show excellent properties such as high quantum efficiency, long persistence of phosphorescence and good stability [5]. Among the techniques used to synthesize luminescent thin films, pulsed laser deposition (PLD) is a unique process for stoichiometric ablation of the target material offering an excellent control of the film morphology [6].

The substrate temperature is among the key deposition parameters in PLD. During PLD, the kinetics of atomic arrangement is mainly determined by the substrate temperature and the energy of the deposition atoms [7]. Additionally, the mobility of the atoms deposited on the surface is directly dependent on temperature, a dependence which can to a large extent influence the activation energy of each process [8].

In our previous report [1] on pulsed laser deposited $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films, the substrate temperature was varied on the range 40-700°C and the best PL was from the film deposited at 400°C. The film deposited at the highest temperature of 700°C gave the poorest PL properties. Similarly, the films prepared on the substrate temperature range of 40-150°C gave poor PL results. Now, since only the monoclinic structure enhances the luminescent properties, the low intensity at higher temperature is most likely due to the existence of the hexagonal phase which does not enhance luminescence [9-10]. Generally, high substrate temperature depositions are discouraged due to the inter-diffusion reaction that takes place at the film/substrate interface of the as-grown films [11].

PLD $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited at intermediate temperatures with good PL properties are of great interest, since they are less costly. The optimum range with reference to our previous report is chosen to be 200-500°C.

In this work, the influence of substrate temperature optimum range (200-500°C) on the morphological, structural and photoluminescence and properties of pulsed laser deposited $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films is presented. The change of elemental compositions with the substrate temperatures is also discussed.

2. Experimental Details

Commercially available $SrAl_2O_4:Eu^{2+}$, Dy^{3+} standard phosphor powders from phosphor technology (UK) were pressed into a pellet and annealed at 600°C in air for about 24 hours to remove water vapour and other volatile from the pellet. The annealed pellet was left to cool for about 6 hours before installing in the PLD system. Silicon (100) wafer substrates were cleaned in an acetone for 5 min, in an ultrasonic water bath and then in methanol for the same time duration. The deposition chamber was pumped by a turbo molecular pump to a base pressure of 8×10^{-6} mbar before the system was backfilled with oxygen ambient gas to a pressure of 343 mTorr. The Lambda Physic 248 nm excimer KrF laser was used to ablate the thin films. The laser fluency, repetition rate and number of pulses were fixed at 0.74 J/cm^2, 8 Hz and 12000 respectively. With all other deposition parameters fixed, films were deposited at substrate temperatures; 200, 350 and 500°C. The ablated area was 1 cm^2 and the laser beam was focused using a 20 cm focal length quartz lens on the rotating target at 45°C angle of incidence. A Shimadzu Super scan SSX-550 system was used to collect the SEM and EDX data. AFM images were obtained from a Shimadzu SPM - 9600. XRD data was collected by using a D 500 diffractometer using CuKα radiation of λ = 1.5405 nm. The excitation source was from the Xenon lamp (λ = 330 nm) of the Cary Eclipse Fluorescence Spectrometer.

3. Results and Discussion

3.1. AFM Results

Figure 1 shows the AFM pictures of the films deposited at different substrate temperatures. The morphology of the film prepared at 200°C was smooth; no grain particles could be identified. Films ablated at temperatures higher than 200°C, showed well defined nanoparticles. This is possibly due to the fact that when the substrate temperature is too low, the atoms, molecules and particles induced by the laser beam may have relatively lower energy to move on the substrate surface, which will slow down the motion and recombination of the defects and vacancies [12].

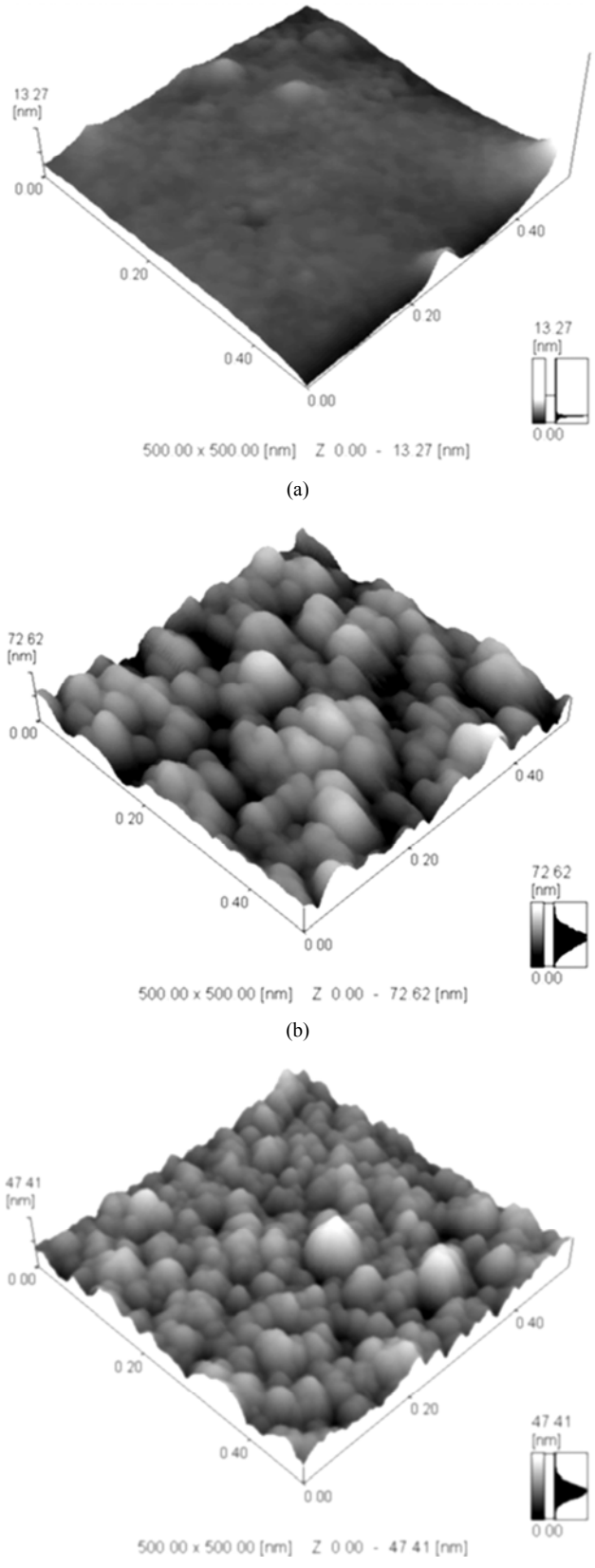


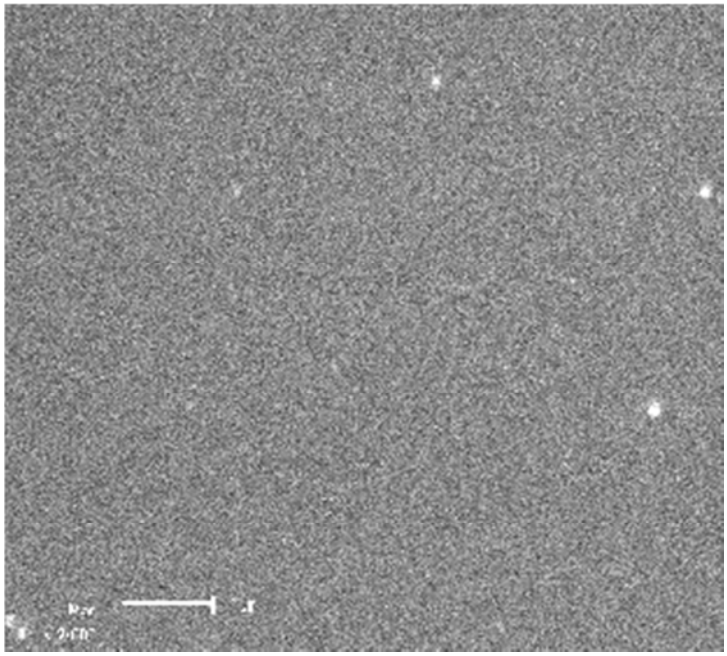
Figure 1. *The AFM images of the PLD $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited at (a) 200°C, (b) 350°C and (c) 500°C substrate temperatures.*

The film deposited at 350°C gave slanted elliptical grain particles, while that deposited at 500°C gave vertically

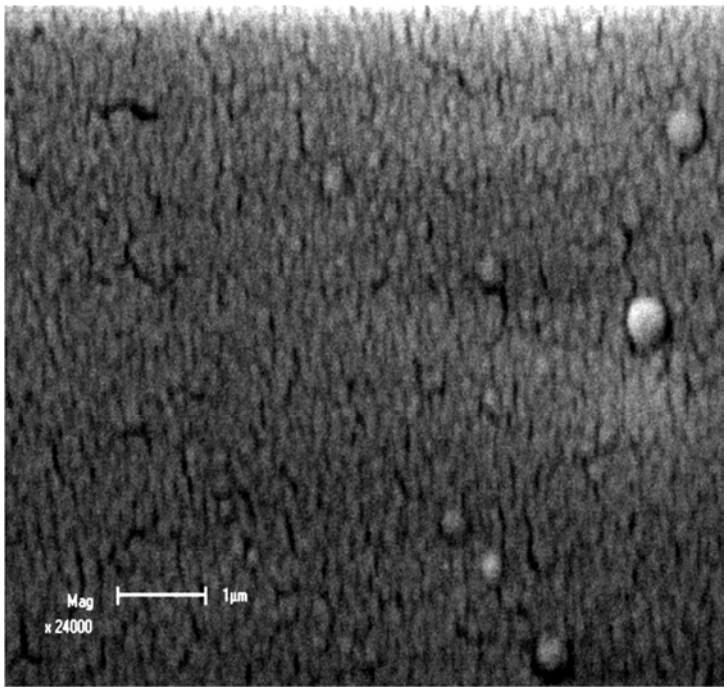
aligned spherical nanoparticles. The nanoparticles of the film deposited at 350°C as observed from the AFM images were almost uniform. However, those of the film deposited at 500°C were greatly varying in sizes. It is reasonable to conclude from the observed AFM images that nanoparticles with well defined grain particles are only possible at substrate temperatures higher than 200°C. The increase in the crystallite size possibly results from the enhancement of the film surface atomic mobility with increasing substrate temperature, which enables the thermodynamically favored grains to grow [12]. This result is similar to the findings reported elsewhere [13] who found that the grain sizes were increasing with the increase in substrate temperatures.

3.2. SEM Results

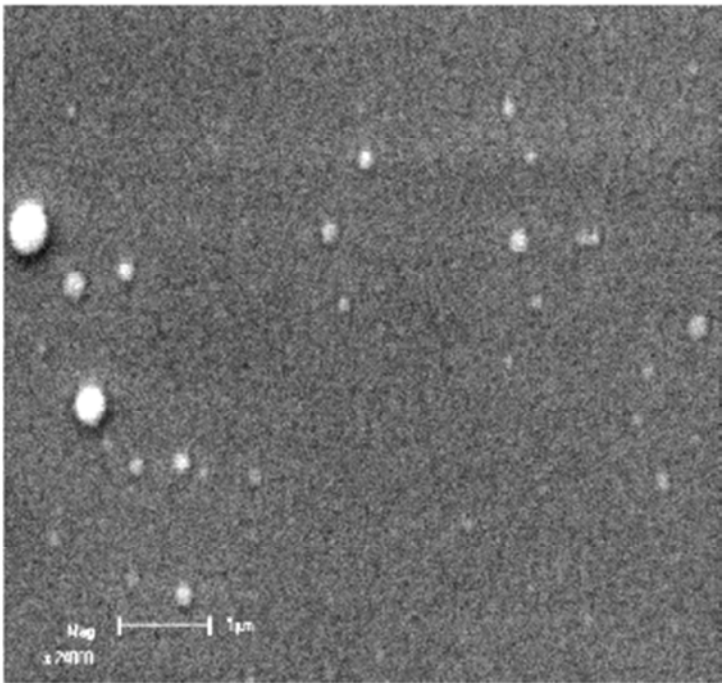
The SEM images for $SrAl_2O_4:Eu^{2+}$, Dy^{3+} films deposited at different substrate temperatures are shown in Figure 2. The surface of the film deposited at substrate temperature of 200°C is smooth, with scanty nano crystallites. The surfaces of the films deposited at temperatures higher than 200°C are rougher than the sample deposited at 200°C with relatively many spherical phosphor crystallites. The roughest surface is recorded by the sample deposited at 350°C.



(a)



(b)



(c)

Figure 2. *SEM images for $SrAl_2O_4:Eu^{2+}$, Dy^{3+} films deposited at (a) 200°C, (b) 350°C and (c) 500°C substrate temperatures.*

Possible explanations for these results are that when the substrate temperature increases, the atomic mobility and diffusion on the surface of the film become strong. The particles can crystallize easily and there are few defects in the films. A high quality of the film can then be obtained. But when the substrate temperatures is high such as 500°C, the adatoms with high kinetic energy collide quickly with each other and are re-evaporated at the same time, a mass of dislocation in the thin film induce the surface of the film coarse [14].

3.3. XRD Results

Figure 3 shows the XRD structures of the ablated films at different substrate temperatures. As it can be observed, all the films gave amorphous structures. This result is similar to those reported elsewhere [4, 15-17], where amorphous structures were obtained for the films deposited at similar temperature ranges.

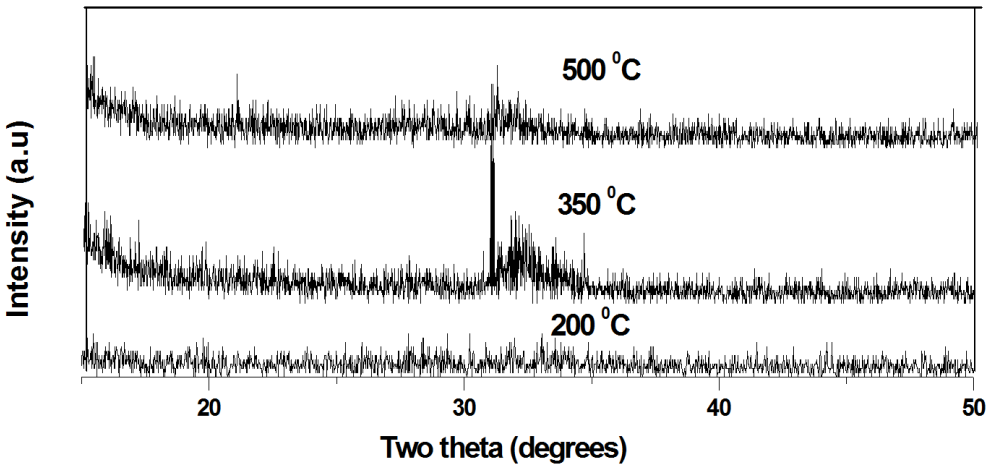


Figure 3. *The XRD crystallographic patterns of the $SrAl_2O_4$: Eu^{2+}, Dy^{3+} films deposited at different temperatures.*

3.4. Photoluminescence Results

Figure 4 shows the variation of PL intensity with the substrate temperature while fixing all other parameters. The films gave a symmetrical green peak at 517 nm resulting from the $^4f_6{}^5d_1 \rightarrow {}^4f_7$ Eu^{2+} transitions and another red peak at 619 nm attributed to $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}. The film deposited at 350°C gave the highest green intensity followed by the film deposited at 500°C. Surprisingly, the film deposited at 200°C gave a higher red peak than a green one. The 619 Eu^{3+} peak has been reported in our previous work

and has been associated with the low laser fluencies [17]. In the same figure, the excitation spectrum is also shown with a peak at 330 nm, which was the excitation wavelength of the films.

The result from this work is contrary to the report from Wako et al. [4], who deposited $SrAl_2O_4:Eu^{2+}$, Nd^{3+} films by PLD technique and varied the substrate temperatures on the 100-300°C range. They observed a decreasing green PL intensity with the increase in the substrate temperature.

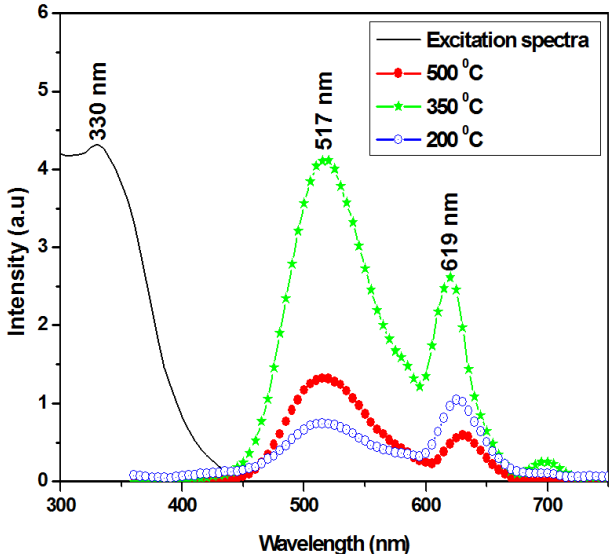


Figure 4. *The excitation and emission spectra for the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited at different substrate temperatures.*

The laser fluency for their work was 0.2 J cm^{-2}, while in the current work is 0.74 J cm^{-2}. The difference in laser fluency and the use of Nd^{3+} rare earth dopant instead of Dy^{3+} and argon atmosphere instead of oxygen atmosphere are possibly the factors behind the differences. Further studies on the mentioned parameters ought to be done to get more understanding of the scientific processes responsible for the differences.

The afterglow characteristics for the same set of films are as shown in Figure 5. The films deposited at temperatures higher than 200°C gave better afterglow characteristics and the highest initial afterglow intensity was deposited at 350°C. The decay constants for the films are listed in Table 1. As expected, that the film deposited at 350°C gave the highest values of the fast (τ_1), medium (τ_2) and slow decay constants (τ_3), consistent with the PL and afterglow data in Figure 4 and 5.

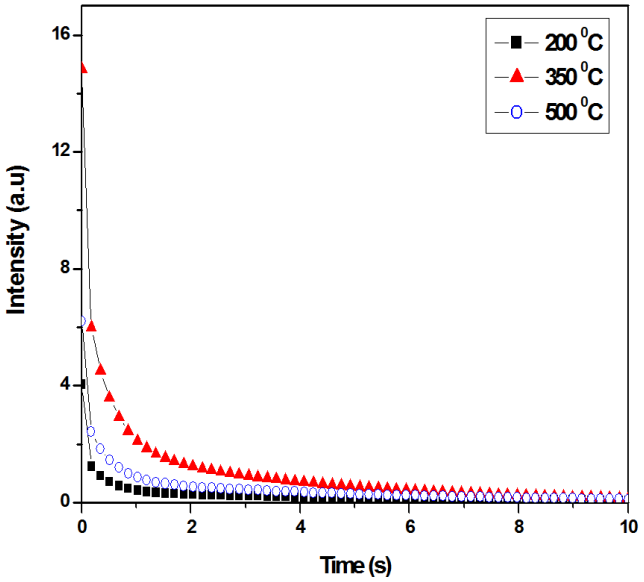


Figure 5. *The afterglow characteristics of the PLD $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited at different substrate temperature.*

Table 1. *Decay constants for monoclinic PLD $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited at different temperatures.*

Substrate Temperature	Decay Constants					
	A_1	A_2	A_3	t_1	t_2	t_3
200°C	2.93	1.34	0.38	0.02	0.38	3.82
350°C	7.91	5.87	2.02	0.04	0.44	5.65
500°C	3.48	2.51	0.77	0.03	0.43	5.21

3.5. EDS Results

Figure 6 shows the EDS results for the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films deposited at different temperatures. All the host elements (Sr, Al and O) of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} material compound were detected by the equipment. However, the dopants could not be detected due to their smaller amounts present in the compound. Silicon (Si) and carbon (C) were also detected. Silicon was coming from the substrate, while carbon was adventitious. As can be observed from the EDS spectra, the films deposited at 200 and 500°C had higher values of Si intensities than the sample deposited at 350°C. This is possibly due to their small film thicknesses. The variation of maximum PL intensity with the elemental weight percentages for the three films was also investigated and the result is as shown in Figure 7. The result shows a direct relationship between the maximum PL intensity and the weight percentages of Al, Sr and O for each film. It is also evident from the PL results that high C contamination leads to low PL intensities.

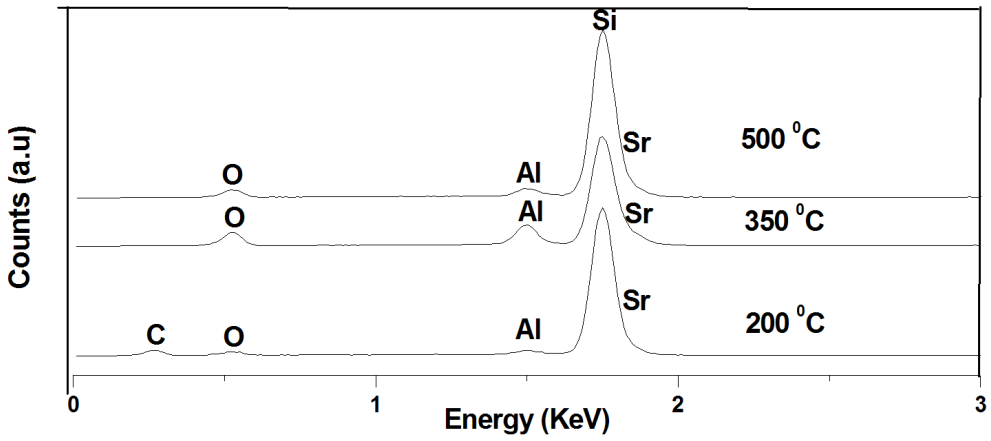


Figure 6. *The EDS results for the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} films deposited at different substrate temperatures.*

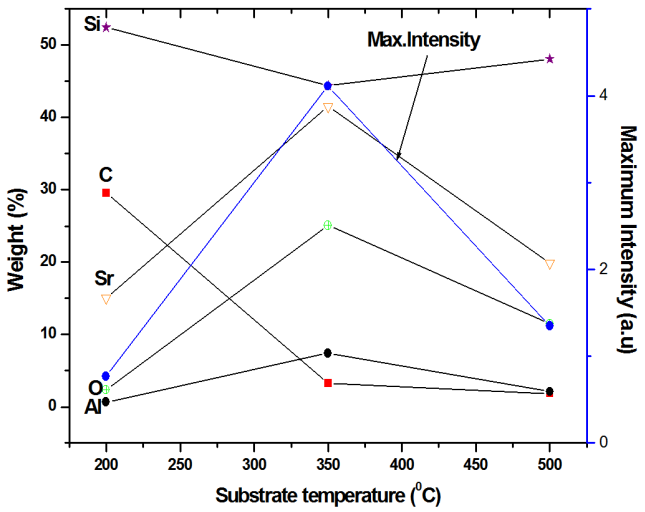


Figure 7. *The variation of substrate temperature with the EDS elemental weight percentage composition and maximum intensity for PLD $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films.*

The film deposited at substrate temperature of 350°C recorded the highest weight percentages of Al, Sr and O and the lowest weight percentage of Si. On the other hand the weight percentage of C was found to decrease with the substrate temperature, signifying that less contamination is only possible at relatively higher temperatures. The analysis of EDS results using the elemental weight percentage composition method gives more insight on the way the elements are varying with deposition parameter and the maximum PL intensity.

4. Conclusion

$SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin films have successfully been prepared using the pulsed laser deposition technique on the optimum temperature range of 200°C - 500°C. The brightest green emission was given by the film that was deposited at 350°C. Films grown at substrate temperatures higher than 200°C recorded higher initial afterglow intensities and superior decay constants. Well defined and packed grains from AFM results are possible only for films deposited at substrate temperatures higher than 200°C. The crystal structure for the as-deposited films was amorphous. The chemical compositions of all the films constitute the main elements of the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} as revealed by the EDS results and the film with the highest PL intensity had higher weight percentages of Sr, Al and O elements. Obtaining a highly emitting $SrAl_2O_4:Eu^{2+}$, Dy^{3+} thin film at 350°C is a great achievement toward low cost and safer depositions of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} through pulsed laser depositions.

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