Effect of Post-annealing on Structural and Photoluminescence Properties of SrS:Dy,Cl Thin Film

E.I. Anila and M.K. Jayaraj
Optoelectronic Devices Laboratory, Department of Physics
Cochin University of Science and Technology, Kochi, Kerala, India, 682 022
mkj@cusat.ac.in

Abstract: *SrS:Dy,Cl thin films are deposited by electron beam evaporation on glass substrates at room temperature and at 300^{0}C.The influence of post deposition annealing in nitrogen and sulfur atmosphere on the structural and photoluminescence emission(PL) properties are investigated. Crystallinity is found to increase with substrate temperature and post deposition annealing. Markable enhancement in PL intensity is also noticed with post deposition annealing in H_2S atmosphere.*

Introduction

Sulfide based phosphors are potential phosphor materials for field emission display applications. Dysprosium activated strontium sulfide has been considered as a promising phosphor for yellow luminescence. Schottky type vacancies are common in ionic bonded semiconductors like SrS. Hence post annealing has got major role to compensate for such vacancies [1].Also post annealing has the effect of lowering the substrate temperature during deposition[2]. Morishita et al reported that post-annealing of cerium activated strontium sulfide in sulfur atmosphere improved the luminance[3]. It is well known from the earlier works that crystalline SrS films can only be deposited at high substrate temperatures either in sulfur atmosphere or with post annealing in sulfur atmosphere at higher temperatures.

In this work an attempt has been made to study the structural and optical properties of SrS:Dy,Cl thin films deposited at room temperature and post annealed in nitrogen and H_2S atmospheres. Also structural properties of films coated at 300^{0}C and then annealed in H_2S atmosphere are studied.

Experiment

SrS:Dy,Cl powder phosphor was prepared by solid state reaction of SrS (99.9% Alfa Aesar) with $DyCl_3$(99.99%, Indian Rare Earths Ltd.), the doping concentration being 0.5%. The mixture was fired at 850^{0}C for 1 hour in H_2S atmosphere. The calcined powder was then made into pellets of 12mm diameter by applying pressure of 2 tonnes and sintered in air with a ramp rate of 0.5^0/minute until 300^{0}C and dwelling at this temperature for 2hours. Thin films were deposited on glass substates at room temperature by electron beam evaporation of the sintered pellets with the substrate to target distance 20cm. The pressure prior to evaporation was about 6x10^{-6}mbar. With an evaporation rate of 10A^0/sec, films of thickness 360nm were deposited. Post deposition annealing was carried out in nitrogen and sulphur atmosphere at 350^{0}C for two hours. The structural characterization of the thin films are performed by XRD analysis using Rigaku diffractometer (CuK_α radiation). The PL emission spectra of the samples were recorded using Spex-Fluoromax-3 Fluorimeter with 150W xenon lamp.

Results and discussions

The crystal structure and preferential orientation of the as-prepared and post-annealed thin film samples of SrS:Dy,Cl is shown in figure1. As prepared samples are amorphous and the crystallinity has improved on post-annealing. The sample annealed in nitrogen atmosphere was oriented along the (200) plane. The film post-annealed in H_2S atmosphere exhibits impurity peaks along with the main peak of SrS but with improved crystallinity.

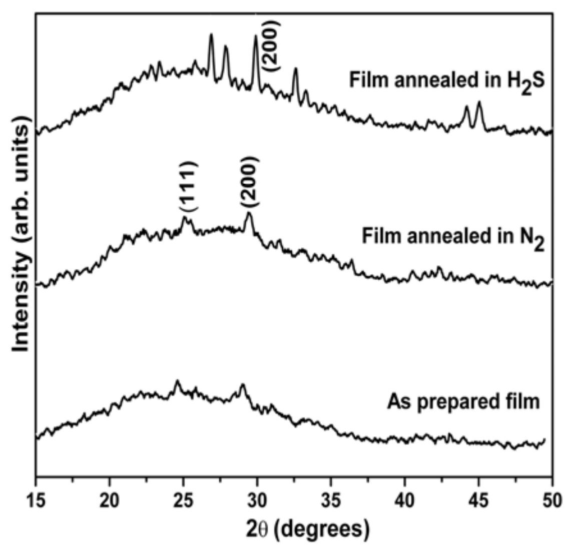

Figure 1. XRD patterns of as-prepared and post-annealed SrS:Dy,Cl thin films

The earlier reports suggest that crystalline films only exhibit better emission characteristics. For SrS, this requires high substrate temperature during deposition. SrS:Dy,Cl thin films deposited at a substrate temperature of 300^{0}C exhibited peaks at (111) and (200) even without post-annealing (Figure 2). Crystallinity was again found to improve on post-annealing the film in H_2Satmosphere at 350^{0}C for two hours. For the annealed sample intensity of (200) peak is 2.9 times as that of unannealed sample. New orientations (220), (311)and (222) also appear on annealing.

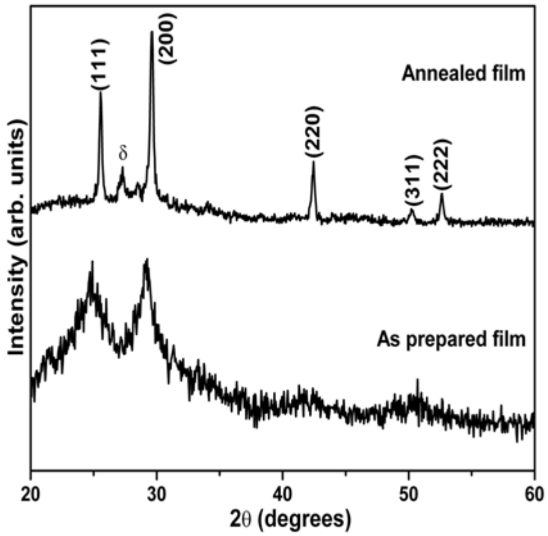

Figure 2. XRD patterns of SrS:Dy,Cl thin film deposited at a substrate temperature of 300^0C and post annealed in H_2S atmosphere for two hours.δ–unidentified peak

The PL emission spectra of SrS:Dy,Cl films recorded at room temperature at an excitation wavelength of 295nm is given in figure 3. The PL emission lines of Dy^{3+} are observed at 485nm ,575nm and 651nm corresponding to the transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{7/2} \rightarrow {}^6H_{5/2}$[4] . The intensity of all the transitions are found to increase with post-annealing. Best PL emission is attained on annealing in H_2S atmosphere. The deposition of the films were done in the absence of background gases in the vacuum chamber which may enhance the formation of sulphur vacancies in the as-deposited film. Post- annealing in H_2S atmosphere might have drastically reduced the concentration of sulphur vacancies in the film in comparison to that post-annealed in nitrogen atmosphere, thereby enhancing the PL intensity.

Conclusion

Substrate temperature and post annealing in H_2S atmosphere improves the crystal structure and orientation.Crystalline SrS:Dy,Cl films are obtained on deposition by electron beam evaporation at a substrate temperature of 300^0C and post annealing the film in H_2S atmosphere at 350^0C for two hours Post annealing in H_2S atmosphere reduces sulfur vacancies thereby enhancing PL emission.

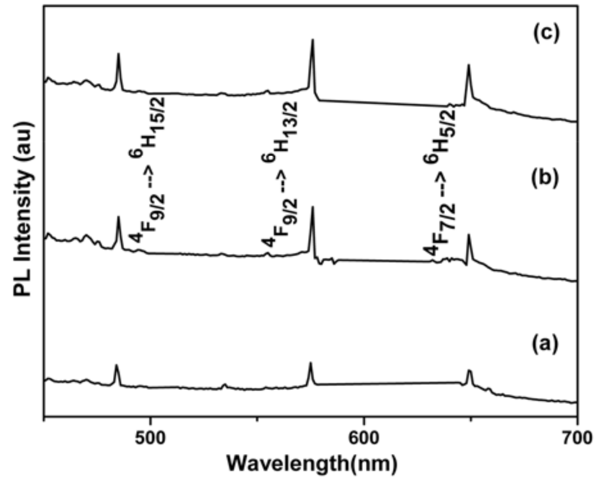

Figure 3. PL emission spectra of SrS:Dy,Cl films at λ_{ex}=295 nm.(a)as prepared film at room temperature (b)film post annealed in N_2 atmosphere at 350^0C for two hours(c) film post annealed in H_2S atmosphere at 350^0C for two hours.

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