Structural and Optical Properties of Ce doped SrS Thin Films Deposited by E-Beam Method

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Abstract—Sulfide based phosphors are potential phosphor materials for field emission display applications. The structural and optical properties of pure SrS and Ce doped SrS thin films are synthesized by e-beam evaporation method is reported. Pure SrS and Ce doped phosphor atmosphere to form thin films on glass substrates. Depositions were conducted on substrates held at room temperature. It was found that both the structure and optical properties of the films are strongly influenced by the deposition and processing parameters. XRD studies confirm both undoped and Ce doped SrS nanoparticles reveal cubic structure. The cubical crystal structure and average crystallite size estimated by X-ray diffractograms are found to lie in nano-range .Surface morphology and elemental composition of the thin films are studied by a field-emission scanning electron microscope (FESEM) and atomic force microscopy (AFM).

1. INTRODUCTION

Nanostructured semiconductors have become the topic of both theoretical and experimental interest in recent time [1]. Alkaline earth sulphide phosphors are well known for their many industrial applications [2]. Strontium sulphide (SrS) semiconductor thin film has great potential for optoelectronic devices fabrication. It has direct wide band gap energy 4.2 eV and this property makes it as a good host material for the visible and infrared emission for various rare-earth ions like Cerium. Cerium is a major element in the useful rare earth family. Pure and Ce doped SrS thin films can be used to develop devices like; optoelectronic devices [3,4], ultraviolet (UV), light emitters [5],solar cells [6] and civil and military applications [7].

SrS thin films have been prepared by variety of thin film deposition techniques such as pulsed-laser deposition [8], RF-magnetron sputtering [9], chemical vapor deposition [10], spray pyrolysis [11], electron beam evaporation [12] and solgel process [13]. The technique used in this work is by the electron beam evaporation deposition (EBED).Electron beam evaporation technique which is one of the most widely used techniques. The deposition rate in this process can be as low as 1 nm per minute.

The aim of this work is to investigate the influence of the preparation condition on structural and optical properties of SrS: Ce prepared by e beam process. The structural characteristics were studied by X-ray Diffraction (XRD), field emission scanning electron microscopy (FESEM) and Atomic force microscopy (AFM) .FESEM and AFM is used to describe the surface morphology of thin film. The optical transmittance was utilized to compute the band gap energy of the films.

2. MATERIALS AND METHOD

The undoped SrS and doped Ce (0.5 mol %) powder for EBED was synthesized by solid state diffusion method in the presence of thiosulfate as a flux [14]. The chemicals used for the preparation were strontium sulfate (SrSO₄), sodium thiosulfate $(Na_2S_2O_3)$, cerium nitrate $[Ce(NO_3)_3.6H_2O]$, ethanol (C₂H₅OH) and activated charcoal, all of analytical grade (99.9%pure). For thin film preparation first the substrates are cleaned with soap solution using a brush and then rinsed by deionized water (DI). Then the substrates are ultrasonicated in acetone for 15 min in a ultra-sonic cleaner. The ultrasonicated substrates are then degreased in methanol in a degreasing unit. Now prepare 5:1:1 solution (DI:H₂O₂:NH₃ Sol) and boil in this solution for 30 min. Keep in DI water for 6 hours and dry in N₂ and put it in glass plate. The distance from target to substrate was fixed at 6 cm and the deposition rate was monitored by a quartz crystal thickness monitor. We have studied the effect of pure SrS and Ce doped SrS thin film. The deposition was done under two different pressures, 4.2 * 10⁻⁵ Torr and 6.4 *10⁻⁶ Torr and at substrate temperatures, in a range of 250°C. The substrate holder was rotated at frequency ~11 Hz during the deposition to produce uniform films. All the samples were stored in complete darkness and in a clean and moisture-free, glovebox (VAC, U.S.A.) environment to prevent them from possible oxidation and/or exposure.

3. RESULTS AND DISCUSSION

3.1. Crystallite structure analysis

The XRD measurements allowed us to determine the orientation of different concentration of Ce-doped SrS nanostructures deposited on the glass substrates. The crystallographic phase and crystallite size of these thin films were been determined using an X-ray diffraction (XRD) technique in which the diffraction angle is varied in the 2θ = $20^{\circ} - 70^{\circ}$ range using CuK $_{\alpha}$ radiation. The diffraction patterns of the samples are representing in Fig. 1. The films were completely oriented along the (111), (200), (220), (311) and (222) planes at $2\theta = 25.5^{\circ}$, 30.5° , 42° , 51° and 53° respectively. This result demonstrates that the thin films have a rock salt cubic structure (PDF card no: 03-065-4281). It can be seen from (Fig. 1) the intensity of the peak is maximum for 0.5mol % of Ce doping concentration. The crystalline sizes of the Ce doped SrS thin films are calculated by using Scherrer formula [15].

$D = k\lambda/\beta \cos\theta$

where K is Scherrer's constant, λ -the X-ray wavelength of Cu-K α radiations(1.54Å), β -the peak width of half-maximum (FWHM) and θ is Bragg's diffraction angle. The average crystallite size is found to be ~ 36nm (undoped) and ~ 54nm.



Fig. 1: XRD images of undoped SrS and Ce³⁺ (0.5mol %) doped SrS thin films

3.2 FESEM analysis

Fig.2 shows the surface morphology of undoped and 5% Ce doped SrS thin films deposited at substrate temperature 250°C. Fig. 2 shows a smooth, uniform grain and spherical like structure. Both films have a similar grain size of \sim 30–60 nm, and the doping concentration has no obvious effect on the grain size. This phenomenon could be explained from the following aspects: on one hand, the grain size would decrease

due to the increase of the dopant atoms, which can exert a drag force on boundary motion and grain growth. [16]



Fig. 2: FESEM images of SrS samples (a) undoped SrS (b) Ce³⁺ (0.5mol %) doped SrS

3.3 AFM analysis

Atomic force microscopy (AFM) is used to study the morphologies of SrS thin films. The surfaces of the films are smooth, continuous and granular structure which will help to minimize the number of conducting paths between the electrode and absorption layer. Fig. 3 shows the 3D AFM images of the thin film nanophosphors. The average grain size estimated with AFM measurement is found to be ~ 16 nm. The root mean square (rms) roughness of the pure SrS and 0.5% Ce-doped SrS thin films were found to be approximately 0.036nm and 0.087 nm, respectively. Our AFM results reveal that the surface roughness decreases with increasing Ce concentrations.



Fig. 3: AFM images of thin films (a) undoped SrS (b) Ce³⁺ (0.5mol %) doped SrS

4. OPTICAL PROPERTIES

Fig. 4 shows the optical transmission of undoped SrS and Ce doped SrS. The decrease in the transmission at about 290–360. The optical transmission of the films is over 80% in the visible region of 400–800 nm, which reveals that the films are highly transparent in the visible region. However, there is a visible change in the band gap absorption edge of SrS:Ce thin films. The absorption edge of undoped SrS film is sharp while that of SrS:Ce film is relatively wide. The absorption coefficient (α) was calculated using [17]

$$\alpha h \nu = A (h \nu - E_g) n$$

Where A is a constant, E_g represents the optical band gap while the exponent n depends on the type of the transition. The optical band gap energy is increases with increase the Ce doping concentration.



Fig. 4: Transmittance spectra of undoped SrS and Ce³⁺ (0.5mol %) doped SrS thin films

5. CONCLUSIONS

The SrS: Ce^{3+} thin films are deposited on glass substrates by EBED method. The structural and optical properties of asdeposited thin films are inter-related to each other. The results based on these films show that the SrS thin film with 0.5 mol% of Ce^{3+} ions concentration has optimum efficiency. Optical measurements indicate that the deposited films have a direct band gap of 4.20 eV which in then confirm the formation of well-crystallized SrS films. The band gap is found to be increases for Ce doped SrS films.

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