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EFFECT OF PRECURSOR VOLUME PROPORTIONS ON SPRAY DEPOSITED EuS THIN FILMS

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Abstract. Europium sulphide (EuS) thin films are successfully deposited on non-conductive bare silicon glass substrates by spray pyrolysis technique at various precursor volume proportions of europium chloride and thaiocatamide. The films were studied by XRD, SEM and UV-Visible spectrometry. The effect of varying precursor volume proportions was studied on morphological and optical properties. The XRD conformed polycrystalline nature. Study enlights the foremost impact of precursor volume proportions on morphological and optical properties.

1. Introduction

Twentieth century has experienced a tremendous development of solid state physics, both in understanding and applications. The birth of quantum theory contributed a great deal to our current understanding of the entire gamut of interesting properties exhibited by bulk solid surfaces. It is now accepted and well known that, the developments in solid state Physics have an incredible impact on industrial sector. Rare earth chalcogenides, in particular, the europium mono chalcogenides, attract considerable experimental and theoretical attention due to their intricate electronic properties relating to the highly co-related f-electrons [1-4]. It is a promising material in the fields of solid state quantum information processing and spintronics. The properties of the europium monochalcogenides EuO, EuS, EuSe and EuTe had found interest for the initial hope of technological applications. Basically the europium sulphide is a ferromagnetic semiconductor [5-7]. Ferromagnetism has been found in several divalent europium compounds. Some of these materials are particularly simple in their crystal and magnetic structure and are ideal for experimental and theoretical study [8-11].

The researchers are concentrating for studying the basic material properties of semiconductors, metals, ceramics and polymers. Europium is a divalent but its compounds can occurs in divalent and also in trivalent configurations [12, 13]. The properties of thin films can be altered by varying precursor volume proportion. The precursor volume proportions have major impact on stochiometry of EuSe thin films [14, 15]. So far the magnetic and electronic properties of europium chalcogenides have been studied widely [16-18]. Several methods of film deposition, such as vacuum evaporation (VE), chemical vapour deposition (CVD), chemical bath deposition (CBD), spray pyrolysis (SP), electro-deposition (ELD) etc. have been employed for the deposition of thin films [19-21]. The grain size at the surface of the films is found to depend on deposition technique also on film thickness [22, 23]. Surface morphology of the films is strongly correlated with the amount of precursor deposited [24-27].

In the present work, spray pyrolysis deposition technique was efficiently employed to prepare europium sulphide EuS thin films by simple, non-vacuum and low cost chemical spray pyrolysis technique (CSP) at various precursor volume proportions. The films have been characterized by SEM, X-ray diffraction (XRD) and UV-Visible spectrometry. The results have been discussed.

2. Experimental

Europium Sulphide (EuS) thin films are deposited onto nonconductive bare silicon glass substrates in an aqueous solution bath containing Europium (III) chloride Eu_2Cl_3 and Thioacetamide CH_3CSNH_2, each of 0.1 M with proportions 1:6, 2:5, 3:4, 4:3, 5:2, and 6:1 of Eu:S, prepared in deionised water in separate beakers as starting solutions. Aqueous solutions of $EuCl_3$ and $CH_3CS.NH_2$ were used as the sources of Eu and S, respectively. The solutions were mixed and stirred well for 50 min, on magnetic stirrer at the rate 475 rotations per minute.

The non conductive bare silicon glass substrates were cleaned with dilute hydrochloric acid (0.1 M), also with the standard laboratory detergent Labonate and again ultrasonically cleaned with double distilled water. The substrates were dried well before deposition by means of hot air spray hand drier for 5 min. The deposition of the film for all the set of solutions was carried out at constant temperature 573 K, on spray pyrolysis equipment (Model No. Holmark HO-TH-04). The substrates temperature maintained with an accuracy of ± 5° C. The other deposition parameters carrier gas air pressure (30 psi), substrate to nozzle distance (15 cm), spray duration (2 min) and precursor quantity (3 ml/min) were kept constant throughout the experiment. The carrier gas was air. All the chemicals used were of analytical reagent grade (99% purity).

3. Results and discussion

3.1. Structural characteristics. The structural characterization of the thin film for all the set of observations was carried out by analyzing the XRD pattern obtained using a X-ray diffractometer model MiniFlex2, with Cu/30kV/15mA and kα radiation (wavelength λ=0.1542 nm), at substrate temperature 573 K are shown in Fig. 1.

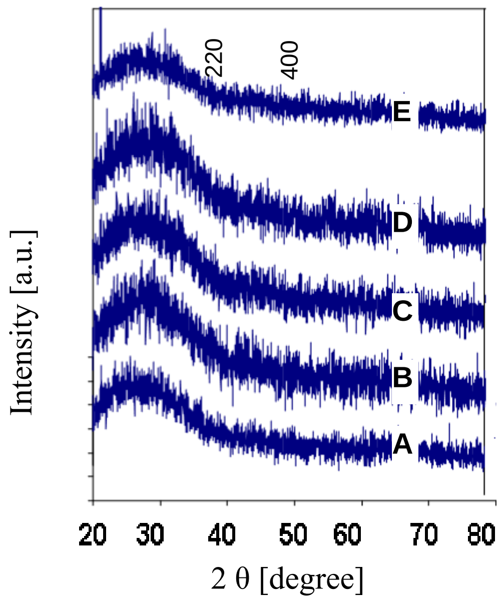

Fig. 1. XRD patterns of EuS thin films deposited for precursor volume proportion of Eu:S from 1:6 to 6:1.

The XRD studies revealed that the spray deposited EuS films are of polycrystalline in nature with cubic structure. The observed diffraction peaks of films are found at 2θ values of 42.394, 42.884, 43.220, and 61.300 corresponding to the hkl planes (400), (220), (220), and (400) respectively.

The different peaks in the diffractogram were indexed and the corresponding values of interplanar spacing '*d*' were calculated and compared with the standard values [28]. The optimum temperature for deposition of good quality EuS thin films is found to be 573 K for all observations. At this temperature, the films are found to be well crystallized as indicated by sharp XRD peaks represented in Fig. 1.

It is found that the deposition temperature 573 K leads to the formation of well crystallized films of spray deposited EuS thin films. The height of (400) and (220) peaks in X-ray diffraction pattern for EuS thin films, deposited at temperature 573 K has observed sharper and FWHM data have resulted in the enhancement of crystallite size in the deposited films at temperature 573 K.

X-ray diffraction patterns of EuS thin films synthesized at substrate temperature 573 K are also analysed by FWHM data and Debye-Scherer formula to calculate the crystallite size of films. The variation of crystallite size with precursor volume proportion of Eu:S from 1:6 to 6:1 for EuS thin films deposited at temperatures 573 K is shown in Fig. 2. From Fig. 2 it is observed that films deposited with above proportion 6:1 are found to have maximum value of crystallite size.

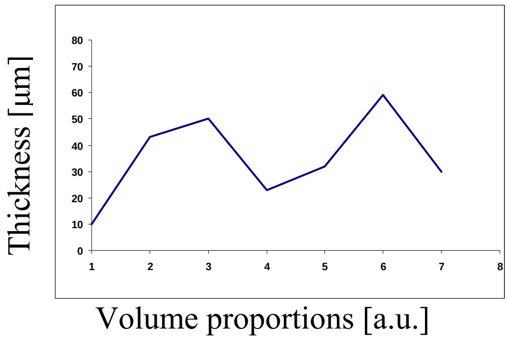

Fig. 2. Variation of crystallite size with precursor volume proportion of Eu:S from 1:6 to 6:1.

3.2. Morphological characteristics. Surface morphology of the samples prepared at substrate temperature 573 K was studied using scanning electron microscope SEM Model: Quanta 200 ESEM System, manufactured by Icon Analytical Equipment Pvt. Ltd, Mumbai. Figure 3 shows the 12000 X magnified micrograph of sample for precursor proportion 1:6 of Eu:S and Figure 4 shows the micrograph of sample for precursor proportion 6:1 of Eu:S.

The SEM images indicate the uniform film deposition and coverage of the substrate by small circular grains. The grain size increases remarkably with highest proportion of Eu in S. The films grown by spray pyrolysis mechanism with increasing volume proportion of Eu demonstrate the increase in coverage deposition area on the flat substrate surface. The 'driving force' of crystal growth in the islands is the gradient of concentration of Eu material, which reaches the surface of glass substrate as spraying flow with carrier gas as air. Since the Ostwald ripening has a certain role in the crystal growth leading to the growth of perfect and bigger crystals [29].

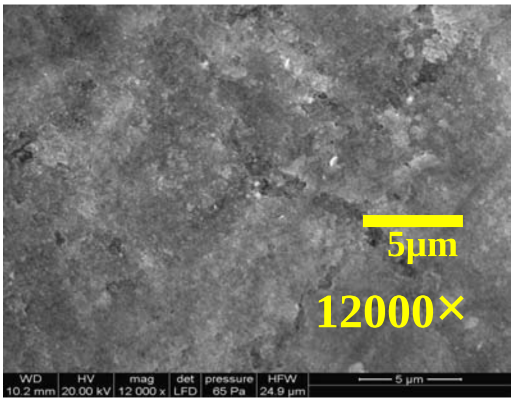

Fig. 3. SEM photograph of EuS thin film for precursor volume proportion 1:6 of Eu:S.

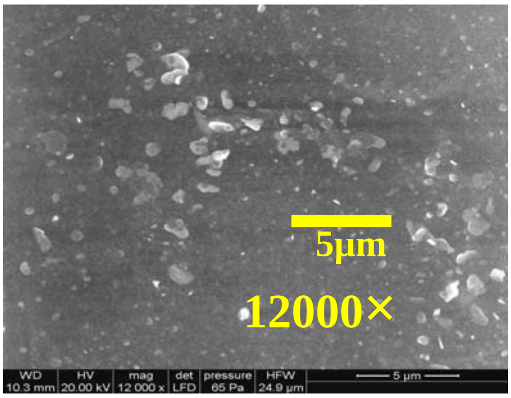

Fig. 4. SEM photograph of EuS thin film for precursor volume proportion 6:1 of Eu:S.

3.3. Optical characteristics. The absorbance and transmission spectra of the five film samples were recorded using Systronics Double Beam UV-Visible spectrophotometer 2201. Optical transmittance measurements of the films were used to estimate the band gap energy from the position of the absorption coefficient edge. The absorption coefficient can be calculated using the relation:

$$\alpha=A(h\nu)^{-1}(h\nu-Eg)^{½},$$

where, A is a constant (slope) and Eg is the energy gap.

From the calculated values of the absorption coefficients a plot of $(\alpha h\nu)^2$ versus $h\nu$ (Tauc's plot), where α is the optical absorption coefficient of the material and $h\nu$ is the photon energy. Extrapolation of the plots to the x-axis gives the band gap energy of the EuS films deposited at 573 K is shown in Fig. 5.

The optical band gap energies of the EuS films deposited at 573 K are found increasing with increase in volume proportion of Eu:S. The plots A, B, C, D, and E are drawn for precursor volume proportions 1:6, 2:5, 3:4, 4:3, and 5:2 respectively. This value is in good agreement with the value reported earlier [30, 31]. The direct band gap energy ranges from

5.68 to 5.95 eV. It reveals that there is makeable increase of band gap more particularly for the highest proportion of Eu in EuS.

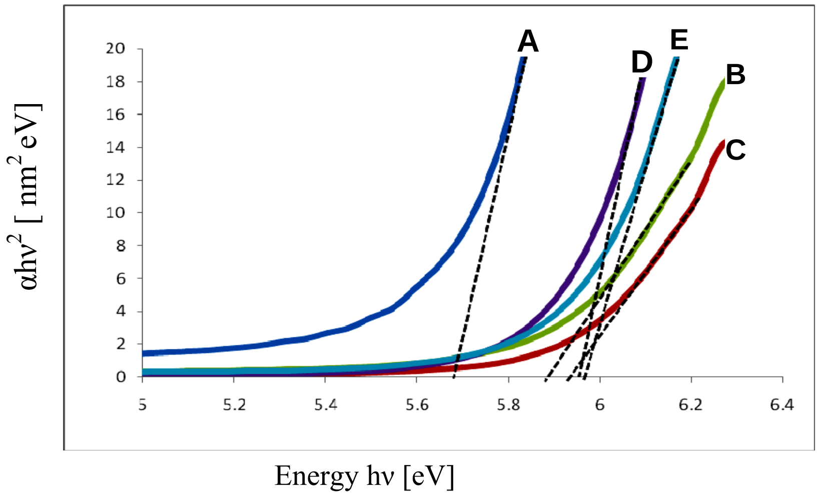

Fig. 5. Plot of $(\alpha h\nu)^2$ versus photon energy at 548 K.

Figures 6 and 7 display the absorption and transmission spectra for EuS thin films.

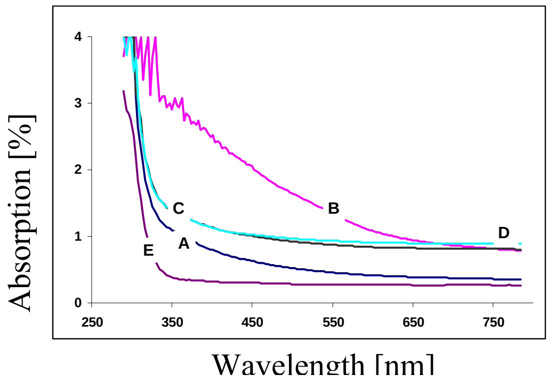

Fig. 6. Absorption spectra of EuS thin films.

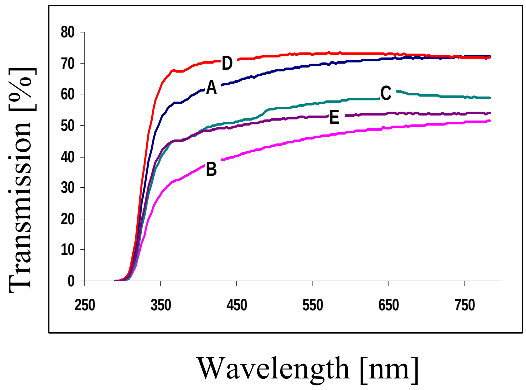

Fig. 7. Transmission spectra of EuS thin films.

Absorption increases rapidly from wavelength 250 nm to 275 nm and it acquires a nearly constant nature beyond 350 nm. The maximum transmission has observed for 5:2 volume proportion of Eu:S and that of minimum for 2:5. Transmission decreases rapidly from wavelength 250 nm to 350 nm and it acquires a nearly constant nature beyond 350 nm. The absorption increases with increase of volume Eu in EuS.

4. Conclusion

The europium chalcogenide (EuS) thin films were successfully deposited by spray pyrolysis technique, on non conductive bare silicon glass substrates with varying precursor volume proportions of Eu:S, from 1:6 to 6:1, at constant substrate temperature 573 K. X-ray diffraction analysis confirmed that the deposition EuS films have a cubic structure. Structural parameters such as thickness of film, crystallite size are calculated and found to depend upon precursor volume proportions. The crystallinity of the films increased with increasing volume proportions Eu:S from 1:6 to 6:1. Optical study indicate that the deposited films have direct band gap energy ranging from 5.68 to 5.95 eV for volume proportions 1:5 to 5:1 of Eu:S. The percentage of absorption was found to increase with increasing volume fraction of the Eu in comparison with S.

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