Global Advanced Research Journal of Agricultural Science (ISSN: 2315-5094) Vol. 1(6) pp. 143-147, August, 2012
Available online http://garj.org/garjas/index.htm

Full Length Research Paper

Morphological and optical study of spray deposited europium chalcogenide thin films

M. M. Betkar*, G. D. Bagde

Physics research Centre, Mahatma Gandhi College, Ahmedpur, Dist. Latur (MS), India- 413515.

Accepted 27 July, 2012

Europium chalcogenide (EuS) thin films have been deposited on non-conductive glass substrates in aqueous solution by spray pyrolysis technique at different substrate temperatures. The films synthesized were studied by XRD, SEM, EDAX and UV-Visible spectrometry. The effect of substrate temperature on morphological and optical properties has been investigated. The XRD studies reveal that the material formed on glass substrates is europium sulphide and of polycrystalline in nature. The grain size for the deposited material is about 171 nm. The SEM studies show that total substrate surface is covered by the film with small grains.

Keywords: band gap; EuS; spray pyrolysis; thin films; XRD

INTRODUCTION

Rare earth compounds attract considerable experimental and theoretical attention due to their intricate electronic properties relating to the highly co-related f-electrons. Europium is a divalent but its compounds can occurs in divalent and also in trivalent configurations. Europium sulphide (EuS) is a well known ferromagnetic semiconductor. Ferromagnetism has been found in several divalent europium compounds. Some of these materials are particularly simple in both crystal and magnetic structure and are ideal for experimental and theoretical study. (Mc Guire TR and Shafer MW 1964) All the europium chalcogenide series have rocksalt structure, the oxide, sulphide, and selenide being ferromagnetic, on these materials the most work has been done. This is especially true of EuS where detailed moment, specific heat and nuclear magnetic resonance measurements are available. The magnetic and electronic properties of europium chalcogenides have been studied widely (Aitken JA et al.,1998; Savne A et al.,2004).

The structural and optical properties of EuS in particular spray deposited EuS thin films have not studied so far. Several methods of the film deposition, such as vacuum evaporation (VE), chemical vapour deposition (CVD), chemical bathdeposition (CBD), spray pyrolysis (SP), electrodeposition (ELD) etc have been employed for the deposition of thin films (Bakry AM 2008). The grain size at the surface of the films are found to depend on deposition technique also on film thickness [5]. Surface morphology of the films is strongly correlated with the amount of precursor deposited (Leea CH et al., 2005; Ashour A 2003). In the present work, spray pyrolysis deposition technique was successfully employed to prepare europium sulphide EuS thin films by simple and low cost chemical spray pyrolysis technique (CSP). The films have been characterized by SEM, EDAX, X-ray diffraction (XRD) and UV-Visible spectrometry. The results have been discussed.

*Corresponding author E.mail:betkarmm@rediffmail.com

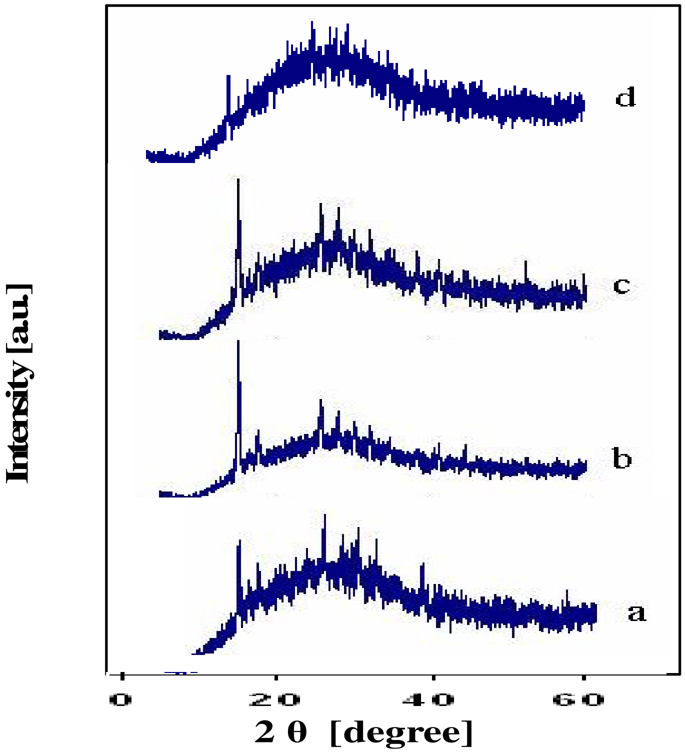

Figure 1 XRD patterns of EuS thin films deposited at substrate temperatures: (a)275ºC, (b) 300 ºC,(c) 325 ºC and *(d) 350ºC*

Experimental

Europium Sulphide (EuS) thin films were deposited onto glass substrates from an aqueous solution bath containing Europium (III) chloride hexahdydrate $EuCl_3$ and Thioacetamide $Ch_3Cs.Nh_2$ each of 0.01 M were prepared in deionised water in separate beakers in proportion 1:1. Aqueous solutions of $EuCl_3$ and $Ch_3Cs.Nh_2$ were used as the sources of Eu and S, respectively. The $EuCl_3$ and $Ch_3Cs.Nh_2$ solutions were mixed for 45 min, well mixed with magnetic stirrer at the rate 550 rotations per minute. The glass substrates were cleaned with dilute hydrochloric acid, standard laboratory detergent and also ultrasonically cleaned with double distilled water. The substrates were dried well before deposition. The deposition of the film was carried out at various temperatures 275 ºC, 300 ºC, 325 ºC and 350 ºC. The deposition was carried out with spray pyrolysis technique (Model No. Holmark HO-TH-04). The other parameters; carrier air pressure (27 psi), substrate to nozzle distance (15 cm), spray duration (2 min) and precursor quantity (2 ml/min) were kept constant throughout the experiment. The carrier gas was air. All the chemicals used were of analytical reagent grade (99% purity).

RESULTS AND DISCUSSION

Structural characteristics

The structural characterization of the thin film 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). X-ray diffraction patterns recorded for the spray deposited EuS films on glass substrates at various temperatures (a) 275 ºC, (b) 300 ºC, (c) 325 ºC and (d) 350 ºC are shown in Figure.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 25.780, 29.920 and 42.460 corresponding to the hkl planes (111), (200) and (220) 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 [8] . The optimum temperature for deposition of good quality EuS thin films is found to be 300 º C. At this temperature the films are found to be well crystallized as indicated by sharp XRD peaks represented in Figure 1 (b). It is found that the deposition temperature 300 ºC, led to the formation of well

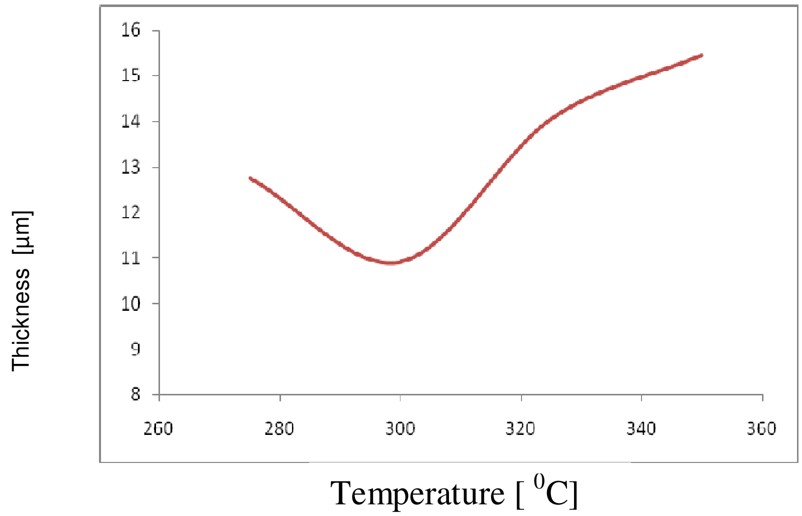

Figure 2. Variation of film thickness with substrate temperature

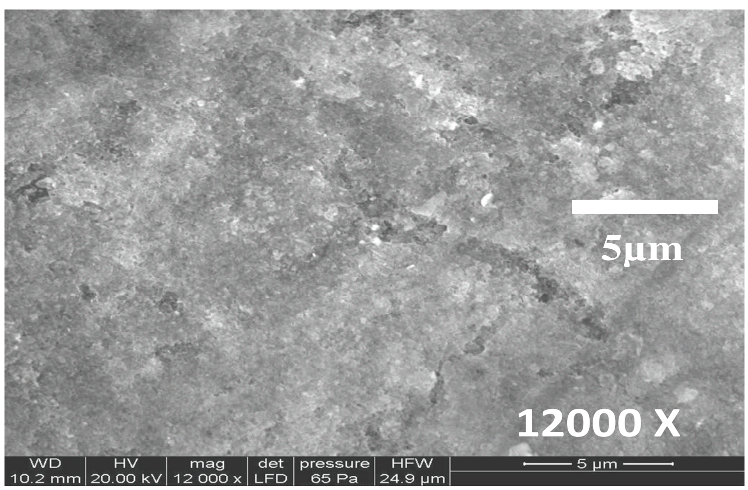

Figure 3. SEM photograph of EuS thin film at 300 ^{o}C

crystallized films. The height of (111) peak in X-ray diffraction pattern for EuS thin films deposited at temperature 300 ºC has observed sharper and FWHM data resulted in the enhancement of crystallite size in the deposited films at temperature 300 ºC.

X-ray diffraction patterns of EuS thin films synthesized at substrate temperatures 275 ºC, 300 ºC, 325 ºC and 350 ºC are also analysed using FWHM data and Debye-Scherrer formula to calculate the crystallite size of films. The variation of crystallite size with substrate temperature for EuS films deposited at temperatures 275 ºC, 300 ºC, 325 ºC and 350 ºC is shown in Figure 2. It is observed from Figure 2, that the crystallite size increases with temperature and films deposited above temperature 300 ºC are found to have maximum value of crystallite size.

Morphological characteristics

Surface morphology of the samples prepared at 300 ºC substrate temperature 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, which indicates the uniform film and continuous coverage of the substrate by small circular

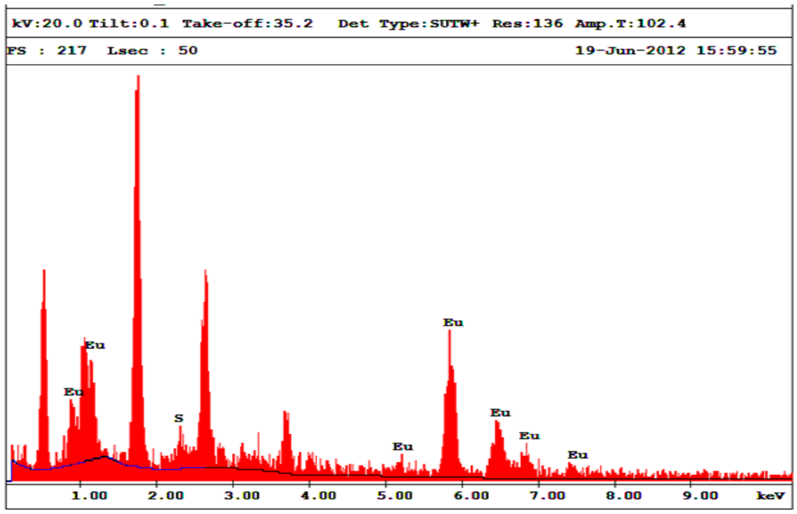

Figure 4 EDAX analysis of EuS thin film at 300 °C

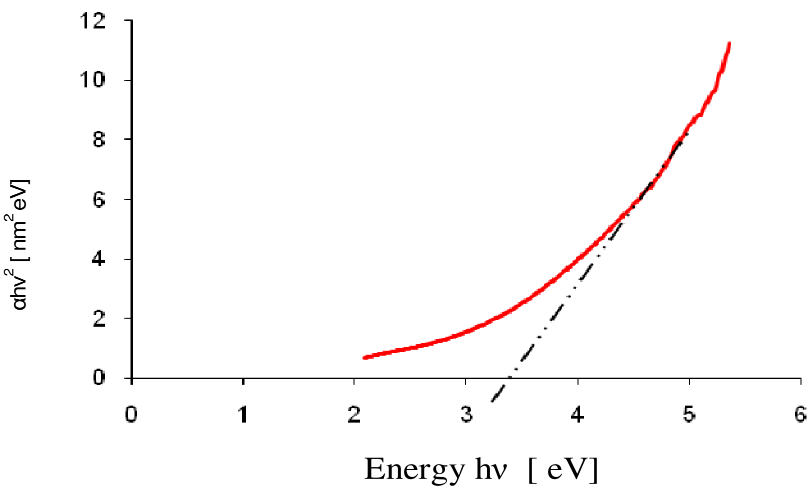

Figure 5 Plot of $(\alpha h\nu)^2$ versus energy hν at 275 ºC

grains. The uniform grain distribution can be seen in the micrograph. As a result these films grow by spray pyrolysis mechanism of experimental solution leading to the very flat surface of the films. The 'driving force' of crystal growth in the islands is the gradient of concentration of the 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 at the expense of more defective and smaller ones (Wagner CZ et al., 1961).

The Figure 4 shows EDAX spectrum of sample of EuS thin film at 300 °C . The peaks of Eu and S are of different intensity. This attributes the doping variation of sulphide in Europium. The evaluated elemental composition for Eu with wt. 95.29 % at 81.00% and that of for S was wt. 4.71 % at 19.00 %. The net intensities for Eu and S was 13.40 and 2.42 respectively.

Optical characteristics

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.

$$\alpha = A/h\nu \, (h\nu - Eg)^{-1/2}$$

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

From the calculated values of the absorption coefficients a plot of $(\alpha hv)^2$ versus *hv* (Tauc's plot), where *α* is the optical absorption coefficient of the material and *hv* is the photon energy. Extrapolation of the plots to the x-axis gives the band gap energy of the EuS films deposited at 275 ºC is shown in Figure 5. The optical band gap energy of the EuS films deposited at 275 ºC is found as 3.1 eV. This value is in good agreement with the value reported earlier (Eastman DE et al., 1969).

CONCLUSION

The EuS thin films were successfully deposited on glass substrates at temperatures 275 ºC, 300 ºC, 325 ºC and 350 ºC by spray pyrolysis technique. 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 varying temperatures. The crystallinity of the films increased with increasing temperature from 275 ºC to 350 ºC. The average sizes of the grains are found to be 6.475 A, which confirm the formation of well-crystallized EuS films . It shows that, the optimized EuS thin film has highly crystallized. Optical transmittance measurements indicate that the deposited films have a direct band gap of 3.1 eV.

REFERENCES

Aitken JA, Cowen JA, Kanatzidis (1998). MG Chem. Mater, 10,

Ashour A (2003). Turk j Physics, 27.

Bakry AM (2008). Egypt. J. Solids, 1 (31).

Eastman DE, Hotzberg F, Methfessel (1969). Physical Review letters, 23 5.

Holroyda J, Idzerda YU (2004). J. Appl. Physics 95, (2004), 11.

JCPDF Diffraction Data Card No.75-0868.

Leea CH, Junga KY, Choib JG, Kangc YC (2005). Materials Sci. and Engr. 116, B, (2005).

Mc Guire TR, Shafer MW (1964). J. Appl. Physics 35, 3.

Savne A, Santi G, Szotek Z, Temmerman WM, Strange P, Horne M, Vaitheeswaran G, Kanchana V, Petit L, Winter H (2004). Phys. Stat. Sol., B14, 241.

Wagner CZ, Electrichem Z , Bunsenges B (1961). Phys. Chem., 65, 581.