Materials Physics and Mechanics 14 (2012) 137-144 Received: July 2, 2012

EFFECT OF COMPLEXING AGENT ON SPRAY DEPOSITED EuS THIN FILMS

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

Physics Research Centre, Mahatma Gandhi College, Ahmedpur,

Dist. Latur (MS), 413515, India

*e-mail: betkarmm@rediffmail.com

Abstract. Complexing agent ethelene-diamine tetra acetic acid (EDTA) (sodium salt) is added in the aqueous solution of Europium chalcogenide (EuS) to deposit thin films on non-conductive glass substrates using spray pyrolysis technique at different substrate temperatures. The films synthesized were studied by XRD, SEM, EDAX and UV-Visible spectrometry. The effect of complexing agent was studied on morphological and optical properties. The XRD studies reveal that the material formed on glass substrates is europium sulphide, films are of polycrystalline in nature. The size for the deposited material is about 200 μm. The SEM studies show that total substrate surface uniformly covered by the film along with cracks.

1. Introduction

Europium sulphide (EuS) is a 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 [1, 2].

Europium is a divalent but its compounds can occurs in divalent and also in trivalent configurations [3]. The properties of thin films can be altered by adding complexing agent. It forms complexes with metal ions. The complexing agent has major impact on stoichiometry of EuSe thin films [4, 5]. So far the magnetic and electronic properties of europium chalcogenides have been studied widely [6, 7]. Several methods of the film deposition, such as vacuum evaporation (VE), chemical vapour deposition (CVD), chemical bath deposition (CBD), spray pyrolysis (SP), electrodeposition (ELD) etc. have been employed for the deposition of thin films [8]. The grain size at the surface of the films is found to depend on deposition technique also on film thickness [9]. Surface morphology of the films is strongly correlated with the amount of precursor deposited [10, 11].

In the present work, spray pyrolysis deposition technique was successfully employed to prepare europium sulphide EuS thin films by simple, non-vacuum and low cost chemical spray pyrolysis technique (CSP) by using complexing agent ethelene-diamine tetra acedic acid (EDTA) (sodium salt) in the precursor solution. The films have been characterized by SEM, EDAX, X-ray diffraction (XRD) and UV-Visible spectrometry. The results have been discussed.

2. 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_3CsNh_2 each of 0.05 M with proportion 1:1, 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 45 min, on magnetic at the rate 600 rotations per minute.

Similarly, another precursor source was prepared with same parameters as above by adding complexing agent EDTA of 0.02 M in proportion 1:1:1, in the precursor. The solution was stirred well for 45 min, on magnetic stirrer at rate 600 rotations per min.

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 for both the set of solutions was carried out at temperatures 275 ºC, 300 ºC, 325 ºC and 350 ºC on spray pyrolysis equipment (Model No. Holmark HO-TH-04). The other deposition parameters; carrier gas 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).

3. Results and discussion

3.1. Structural characteristics. The structural characterization of the thin film for both 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 $\lambda = 0.1542$ nm). X-ray diffraction patterns recorded for the spray deposited EuS films without addition of complexing agent, at substrate temperatures (a) 275 ºC, (b) 300 ºC, (c) 325 ºC, and (d) 350 ºC are shown in Fig. 1.

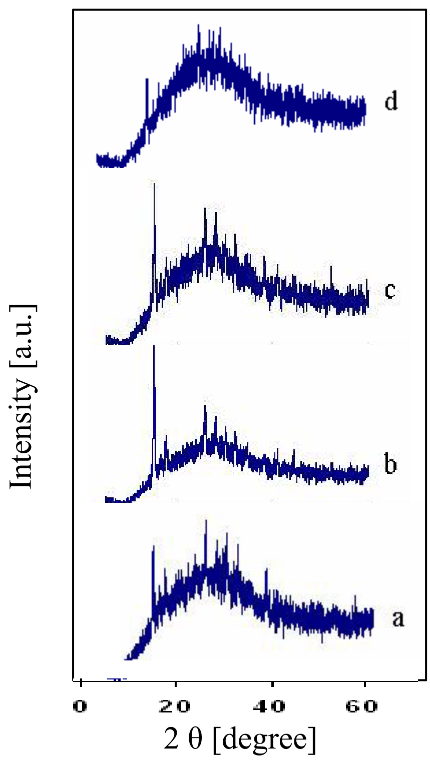

Fig. 1. XRD patterns of EuS thin films deposited without addition of EDTA.

X-ray diffraction patterns recorded for the spray deposited EuS films with addition of complexing agent EDTA, at substrate temperatures (a) 275 ºC, (b) 300 ºC, (c) 325 ºC, and (d) 350 ºC are shown in Fig. 2.

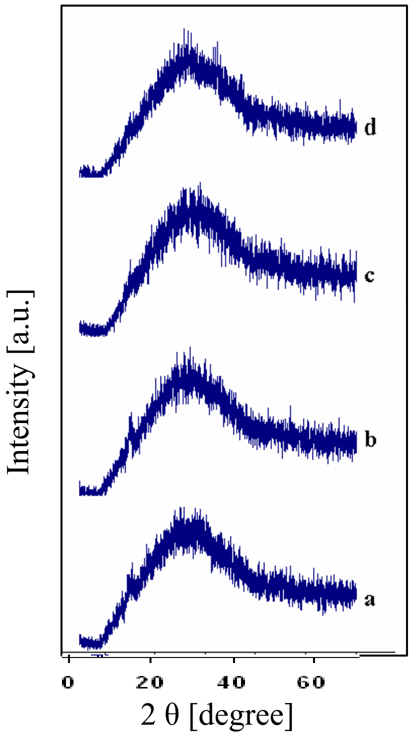

Fig. 2. XRD patterns of EuS thin films deposited with addition of EDTA.

The XRD studies revealed that the spray deposited EuS films are of polycrystalline in nature with cubic structure. The observed diffraction peaks of films without addition of EDTA are found at 2θ values of 25.780, 29.920, and 42.460 corresponding to the hkl planes (111), (200), and (220) respectively.

The observed diffraction peaks of films with addition of EDTA are found at 2θ values of 25.680, 29.000 and 29.120 corresponding to the hkl planes (211), (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 [12]. The optimum temperature for deposition of good quality EuS thin films is found to be 300 ºC for observations both without addition of EDTA. Similarly on adding EDTA the optimum temperature for good quality of thin films is found to be 300 ºC. At this temperature the films are found to be well crystallized as indicated by sharp XRD peaks represented in Fig. 1(b) and Fig. 2(b) without addition of EDTA and addition of EDTA respectively. It is found that the deposition temperature 300 ºC, led to the formation of well crystallized films of spray deposited EuS thin films for and that of 300 ºC with EDTA**.** The height of (111) peak and (200) in X-ray diffraction pattern for EuS thin films without EDTA and with EDTA respectively, 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 without and with addition of EDTA are synthesized at substrate temperatures 275 ºC, 300 ºC, 325 ºC, and 350 ºC and the XRD-patterns are also analysed by 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 without addition of EDTA is shown in Fig. 3 and that of with addition of EDTA is shown in Fig. 4. The average size of the grains without addition of EDTA is found to be 12.75 Å and that of with addition of EDTA is 6.425 Å. It is observed that, thin value of crystallite size decreases abruptly and becomes one half as observed at without addition of EDTA.

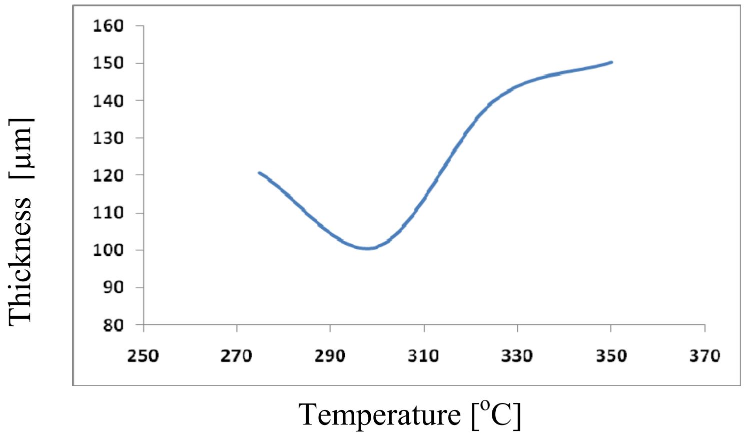

Fig. 3. Variation of film thickness with substrate temperature.

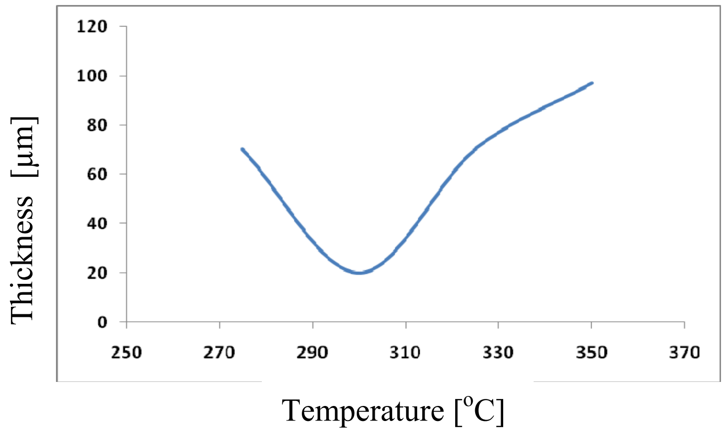

Fig. 4. Variation of film thickness with substrate temperature.

3.2. 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 5 shows the 12000 X magnified micrograph of sample without addition of EDTA, and Figure 6 shows that of with EDTA. The SEM images indicate the uniform film and continuous coverage of the substrate by small circular grains without addition of EDTA, but while adding EDTA, the film shows major cracks. As a result these films grow by spray pyrolysis mechanism of experimental solution leading to the very flat surface of the films and major cracks if added with EDTA. 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 along with major cracks [13].

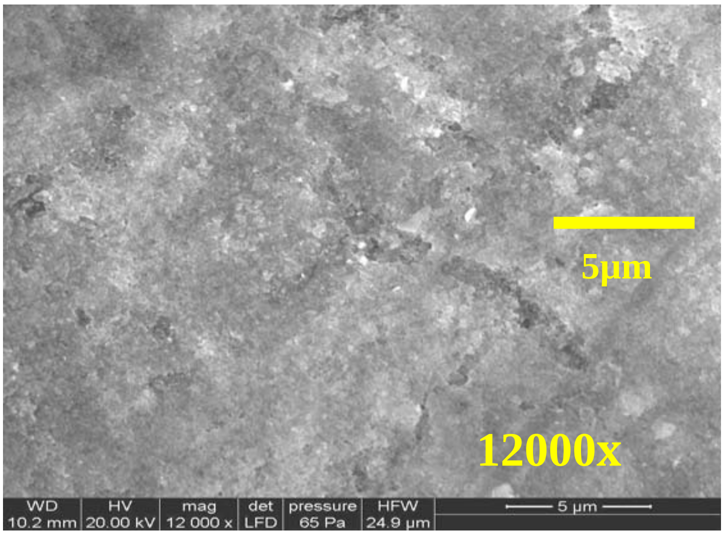

Fig. 5. SEM photograph of EuS thin film without addition of EDTA at 300 ^{o}C.

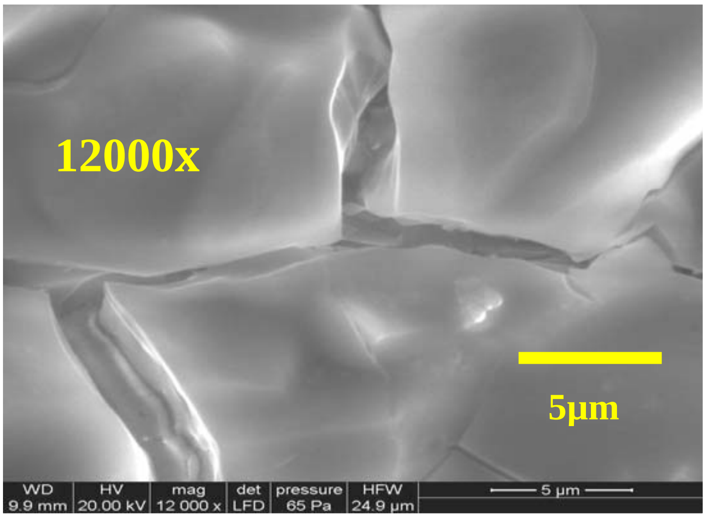

Fig. 6. SEM photograph of EuS thin film with addition of EDTA at 300 ^{o}C.

Figure 7 and Figure 8 show EDAX spectrums of sample of EuS thin film at 300 ^{o}C, without and with addition of EDTA respectively. The peaks of Eu and S are of different intensity. This shows the doping variation S in Eu. The evaluated elemental composition without addition of EDTA is observed and for Eu with wt. 95.29 % at 81.00 % and that of for S was wt. 4.71 % at 19.00 %. It is observed that the doping percentage increases with addition of complex agent in precursor. The net intensities for Eu and S were 13.40 and 2.42 respectively. The evaluated elemental composition with addition of EDTA is observed and for Eu with wt. 98.23 % at 92.11 % and that of for S was wt. 1.77 % at 7.89 %. The net intensities for Eu and S were 34.30 and 2.20 respectively. The addition of EDTA decreases the doping percentage. It revels that EDTA can be added to optimise the doing percentage.

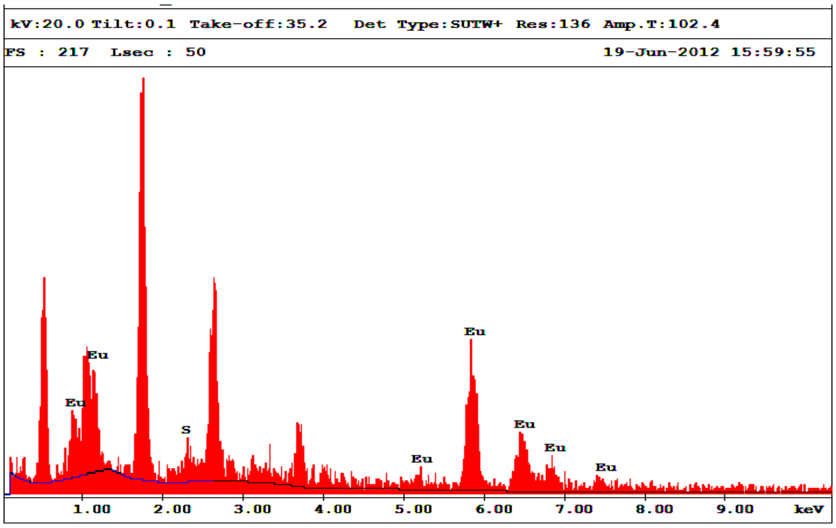

Fig. 7. EDAX analysis of EuS thin film without addition of EDTA at 300 °C.

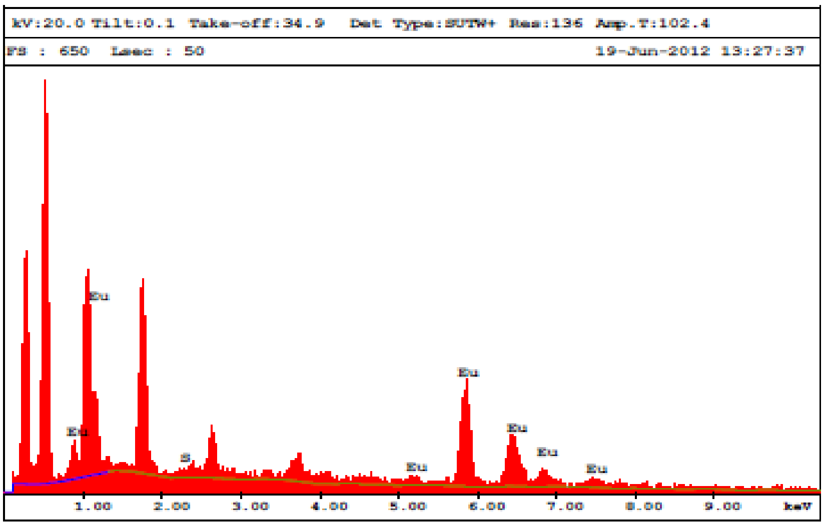

Fig. 8. EDAX analysis of EuS thin film with addition of EDTA at 300 °C.

3.3. 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:

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

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

From the calculated values of the absorption coefficients a plot of $(\alpha h\nu)^2$ 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 without addition of EDTA, deposited at 275 ºC is shown in Fig. 9. 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 [14]. Figure 10 shows the extrapolation of the plots to the *x*-axis gives the band gap energy of the EuS films with addition of EDTA, deposited at 275 ºC is found as 6.0 eV. It reveals that there is makeable increase of band gap more particularly, the band gap becomes twice.

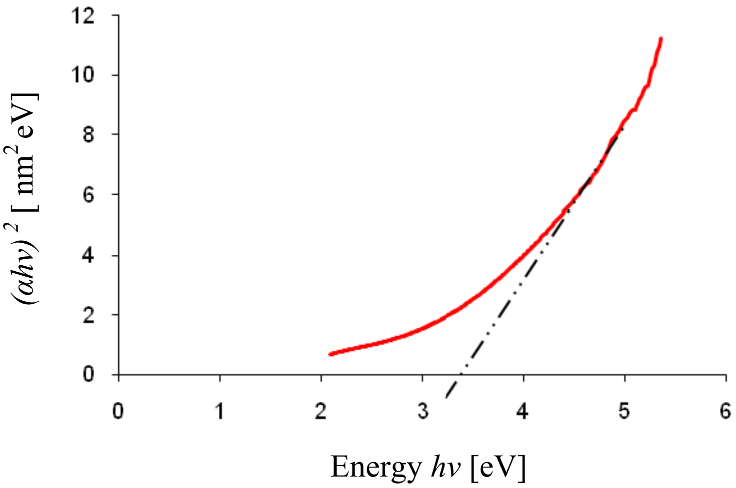

Fig. 9. Plot of $(\alpha hv)^2$ versus energy hv at 275 ºC.

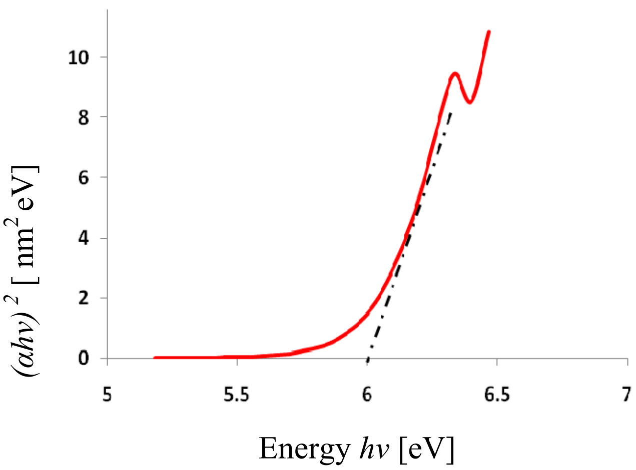

Fig. 10. Plot of $(\alpha hv)^2$ versus energy hv at 275 ºC.

4. Conclusion

Without addition of complexing agent EDTA and with addition of complexing agent EDTA 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 cubic structure. Structural parameters such as thickness of film, crystallite size are calculated and found to depend upon complexing agent EDTA. The crystallinity of the films decreased with addition of complexing agent EDTA. The average size of the grains without addition of EDTA is found to be 12.75 Å, and that of with addition of EDTA is 6.425 Å, which confirm that the crystal size becomes nearly half. The study reveals that, thin film has highly crystallized. Optical transmittance measurements indicate that the deposited films without addition of EDTA have the direct band gap of 3.1 eV and the direct band gap with addition of EDTA is 6.01 eV.

Acknowledgements
One of the authors MMB is thankful to University Grants Commission, New Delhi, India, for the award of Teacher Fellowship under 'Faculty Improvement Programme', and also thankful to S.R.T. M. University recognized, Physics Research Centre, Mahatma Gandhi College, Ahmedpur, Dist. Latur, for providing research facility in spray deposited thin films.

References
[1] Raymond L. Kallaher, *Electron Tunneling Transport Across Heterojunctions Between Europium Sulfide and Indium Arsenide* (*Ph.D. Thesis, Florida State University, USA,* 2007).
[2] M.M. Betkar, G. D. Bagde // *Materials Physics and Mechanics* **14** (2012) 74.
[3] T.R. McGuire, M.W. Shafer // *J. Appl. Phys.* **35** (1964) 3.
[4] Kuniaki Murase, Takeshi Honda, Masaki Yamamoto, Tetsuji Hirato, Yasuhiro Awakura// *J. Electrochem. Soc.* **148** (2001) C203.
[5] I.I. Boone, T.P. Vandoern, A.K. Berry // *Thin Solid Films* **87** (1982) 259.
[6] J.A. Aitken, J.A. Cowen, M.G. Kanatzidis // *Chem. Mater.* **10** (1998) 3928.
[7] A. Savne, G. Santi, Z. Szotek, W.M. Temmerman, P. Strange, M. Horne, G. Vaitheeswaran, V. Kanchana, L. Petit, H. Winter // *Phys. Stat. Sol. B* **14** (2004) 241.
[8] J. Holroyda, Y.U. Idzerda // *J. Appl. Phys.* **95** (2004) 11.
[9] A.M. Bakry // *Egypt. J. Solids* **1** (2008) 31.
[10] Chang Hee Lee, Kyung Youl Jung, Joong Gill Choi, Yun Chan Kang *// Materials Science and Engineering: B* **116** (2005) 59.
[11] A. Ashour *// Turk. J. Physics* **27** (2003) 551.
[12] JCPDF Diffraction Data Card No.75-0868.
[13] C.Z. Wagner // *Z. Electrichem.* **65** (1961) 581.
[14] D.E. Eastman, F. Holtzberg, S. Methfessel // *Phys. Rev. Lett.* **23** (1969) 226.