Morphological Studies on Europium Selenide Thin Films

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***Abstract*—The Europium Selenide thin films are deposited on silicon, non-conductive glass substrates. The films are deposited by simple non-vacuum Spray Pyrolysis technique. The deposition was carried at increasing substrate temperature and changing the in aqueous precursor medium. The synthesized thin films were studied morphologically and optically. The XRD reveals the Nature of thin films.**

***Index Terms*—EuSe, thin films, spray pyrolysis, aqueous, XRD, SEM**

I. Introduction

Any solid or liquid system possesses at most two-dimensional order of periodicity is called 'thin film'. The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical, properties has changed the modern society. There is an increasing technological progress. Modern technology requires thin films for various important applications The advancements in micro-technology and the evolution of new nonmaterial and devices have been playing a key role in the development of very accurate and reliable devices. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behaviour of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film.

When we consider a very thin film of some substance, we have a situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in a profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. The thin film technology have developed tremendously in the last few years owning many scientific achievements from various experiments, offering newer challenges and opportunity to the quest for every smaller devices on molecular level has gained the focus of attention of the scientific community [1]-[5]. The group of europium chalcogenide (EuO, EuS, EuSe and EuTe) belongs to the most intensively investigated materials because of their simple NaCl structure and interesting magnetic, optical and semiconducting properties. These are classified as magnetic semiconductors. Of those EuS and EuO are ferromagnetic with Curie temperature below 70 and 17 K respectively, while EuSe is a more complex system showing both ferromagnetic and anti-ferromagnetic ordering within 5.5–1.8 K. The researchers reported studies on europium chalcogenides for depositions and characterisations. Broad object of this research work is to synthesize and to study the characteristics of europium chalcogenide thin films, deposited by spray pyrolysis technique.

The general object of this research work is to synthesize and to study the morphological characteristics of europium selenide thin films, deposited by spray pyrolysis in aqueous precursor mediums [6]-[10].

The deposition techniques have great impact on the physical and electrochemical properties of thin films such as morphology, structural, and characterizations. The synthesizing parameters which in turn make the films suitable or a particular application [11]-[14]. In modern material science specific surface properties therefore gain increasing importance. The type of device, geometry and the performance expected are the key terms to choose an appropriate technique. Present study concentrates on the properties of europium selenide (EuSe) thin films by spray pyrolysis deposition.

A number of thin film deposition are available, such as vacuum evaporation , chemical vapor deposition , chemical bath deposition , spray pyrolysis (SP), electro-deposition etc. have been used for thin films deposition . The size of grains and thickness of synthesized films is found to depend on the technique of deposition. The amount of precursor deposited effects on surface morphology [15], [16].

The morphological characterizations of the deposited samples are undertaken.

II. Experimental

Optimization of parameters: The film deposition by spray pyrolysis is carried out at the optimizes parameters. The spray rate, substrate temperature, concentration of

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spraying solution, Eu:Se ratio parameters are optimized.

Spray rate: It is one of the important parameters in the thin film deposition. It is varied by changing the pressure on carrier. During the deposition process, it was maintained 3 psi.

Substrate temperature: To optimize the substrate temperature, the mixed equimolar precursor of $EuCl_3$ and selenium dioxide SeO_2 with Eu:Se volume ratio 50:50 of concentration 0.01 M is sprayed with spray rate 2 ml/min onto the experimental substrates maintained at temperatures between 423 to 648 K with interval of 25 K with ±2 K accuracy. The variation of EuS film thickness with substrate temperature was studied. It is observed that the EuSe film at 573 K has maximum thickness. The decrease in thickness below 573 K may be due to complete thermal decomposition. The EuSe films prepared at optimized temperature 573 K are well uniform and well adherent to the substrates.

Concentration of spraying precursor: The film properties are also depends upon spraying precursor concentration. To optimize the concentration of precursor, the substrate temperature was kept at constant value 573 K. The films were prepared at 0.002, 0.004, 0.006, 0.008, 0.01, 0.02. And 0.04 M concentrations of $EuCl_3$. The spray rate was maintained at 2 ml/min. Plot of variation of EuSe thin film thickness with precursor concentration was studied. It was found that, the films prepared at 0.01 M concentration are of considerable higher thickness. The 0.01 M concentration is employed as optimized value of precursor concentration.

Eu: Se volume ratio: The variation in volumetric proportion of experimental precursors significantly affects the properties of deposited material, may be the effective method for controlling the properties. With a view to optimize the composition of Eu:Se volume ratio, the films were prepared at various volume compositions as 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10, at optimized substrate temperature of 573 K and precursor solution concentration of 0.01 M with spray rate 2 ml/min and at pressure 3 psi. The variation of film thickness with Eu:S volume ratio was studied. It is seen that, below and above 50:50 composition the film thickness is lower may be due to incomplete reaction. Therefore, 50:50 is the optimized composition of EuSe film deposition. Spray pyrolysis is a simple technique in which no high quality substrates are required. Thin films of europium selenide (EuSe) were deposited onto glass substrates from an aqueous and non-aqueoues solution bath containing europium (III) chloride hexahdydrate $EuCl_3$ and selenium dioxide SeO_2 each prepared in deionised water and methanol in separate beakers in equal stoichiometric volume proportions 1:1. Europium (III) chloride hexahdydrate $EuCl_3$ and selenium dioxide SeO_2 were used as a source of Eu and Se to form EuSe thin films. The aqueous solution was well stirrered by employing magnetic stirrer equipment at the rate 550 rpm for 45 min.

Thin films were deposited onto glass substrates, non-conducting bare and by varying concentration of precursor and temperatures of glass substrate. The temperature was maintained with an accuracy of ±5 °C. The pressure of carrier gas air (3 psi), distance of substrate to nozzle (15 cm), duration of spray (2 min) and precursor quantity (3 ml/min) were kept constant throughout the experiment. All the chemicals used were of analytical reagent grade (99% purity).

Synthesized EuSe film samples at preparative parameters are summarized in following Table I.

TABLE I. PREPARATIVE PARAMETERS OF EUSE THIN FILMS

Precursor Medium	Normality $EuCl_3$ / SeO_2 in M	Substrate Temperature in K
Aqueous	0.001/0.01	(a) 548, (b) 573, (c) 598, (d) 623
	0.01/0.05	

The morphological characterization is the most important factors for a reliable and outstanding performance of semiconductor devices. In the upcoming literature those properties of the deposited material onto substrate samples are outlined with their important findings.

Structural characterization: The EuSe thin films were successfully deposited onto glass substrates in aqueous precursor medium at temperatures (a) 548, (b) 573, (c) 598 and (d) 623 K; non-aqueous precursor medium at temperatures (a) 373, (b) 398, (c) 423 and (d) 448 K, by spray pyrolysis technique. Structure of thin films depends on a technique of their deposition. The films are analyzed for their structure and thickness calculations.

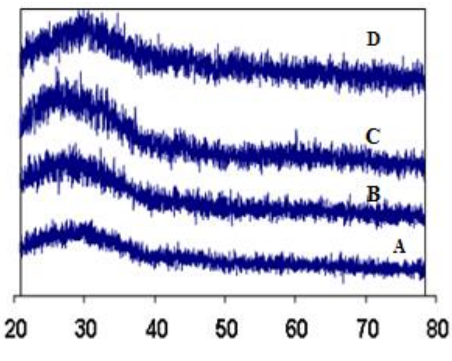

Figure 1. XRD pattern of EuSe thin films

XRD pattern of EuSe film samples: X- ray diffraction (XRD) is used for two reasons, one for information about crystllographhic properties of the material and secondly for determining the thickness of thin layers. It is well known fact that a single crystal has perfect long range order throughout the sample in all dimensions, whereas, an amorphous material has entirely no long range order. In between these two extreme cases, a polycrystalline film has limited long range order, but the structure does not extend throughout the film and, thus, a polycrystalline film can be thought of being made up of small, randomly orientated crystallites on the film surface. In present work 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/30 kV/15mA and kα radiation (wavelength λ=0.1542 nm). X-ray diffraction patterns recorded for the spray deposited EuSe films are shown in following Fig. 1.

The complex phased peaks indicate well crystallized EuSe thin films. This conforms the polycrystalline nature of EuSe films as simple cubic structure. The optimized temperature for deposition of good quality EuSe thin films is found to be 573 K. The height of (220) peak in X-ray diffraction pattern for EuSe thin films deposited at temperature 573 K has found more sharper and FWHM data conforms the improvement of crystallite at temperature 573 K. X-ray diffraction patterns of EuSe thin films is evaluated using FWHM data and Debye-Scherrer formula for the calculation of the crystallite size of EuSe films synthesized at substrate temperatures 548 K, 573 K, 598 K and 623 K.

Morphological characterization: Scanning electron microscope (SEM) study of synthesized film sample was produced by using scanning electron microscopy (SEM Model: Quanta 200 ESEM System, manufactured by Icon Analytical Equipment Pvt. Ltd, Mumbai) to assess the quality of the europium selenide (EuSe) thin films. The Fig. 2 shows SEM images of EuSe film sample. The composition of the films was investigated using an energy dispersive analysis by X-rays (EDAX Model: Quanta 200 ESEM System, manufactured by Icon Analytical Equipment Pvt. Ltd, Mumbai).

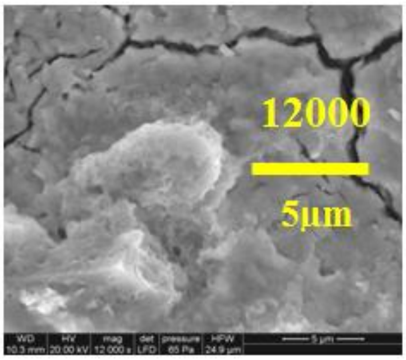

Figure 2. SEM image of EuSE thin films

III. Results and Discussions

XRD Analysis: X-ray diffraction patterns recorded for the spray deposited EuSe thin film sample shown in Fig. 1 revealed that the spray deposited EuSe films are of polycrystalline in nature with cubic structure and face centered lattice arrangement.

The peaks in a X-ray diffraction pattern are directly related to the atomic distances. The observed diffraction peaks of films are found at 2θ values of 28.880, 41.260 and 48.240 corresponding to the hkl planes (200), (220) and (311) respectively. The peaks in the diffractogram were indexed and the corresponding values of inter-planar spacing d were calculated and compared with the standard values JCPDF Diffraction Data Card No.74-1343. The optimum temperature for deposition of good quality EuSe thin films is found to be 573 K. At this temperature the films are found to be well crystallized as indicated by sharp XRD peaks. It conforms that, the deposition temperature 573 K led to the formation of well crystallized thin films [17].

SEM Analysis: The micrographs recorded with uniform distribution of grains size over total coverage of the substrate with a compact and fine grained morphology. At temperature 573 K, there is an increase in nucleation over growth and the film surface is covered with uniform grain without pinholes as seen in SEM images. The Fig. 2 shows SEM images of EuSe film sample at increasing x level. It conforms the deposition of Eu and Se. The elemental analysis was also carried out for Eu and Se. The average atomic percentage of Eu:Se was1:8. It is observed that, the metal stoichiometry of the EuSe thin films synthesized by present technique is nearly identical to the stoichiometry of the starting elements [18].

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