

Morphological Studies on Europium Oxide (EuO) Thin Films

Maheshwar Mallikarjun Betkar^{1,*} and Angad Nagorao Jadhav²

¹Shri Kumaraswami Mahavidyalaya, Ausa, Dist. Latur-413520, MS, India

²Yeshwant Mahavidyalaya, Nanded- 431602, MS, India

*Corresponding author

Abstract—Europium Oxide thin films were deposited onto non-conductive clean bare glass substrates. The prepared precursor was in equal stoichiometric volume proportions in aqueous and non-aqueous mediums. The morphological, structural characteristics of the deposited samples were undertaken.

Keywords—Thin Films; EuO; XRD; SEM; EDAX

I. INTRODUCTION

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.

The family of europium monoxide (EuO) based materials have been also recently investigated for spintronic related research. Stoichiometric EuO is a paramagnetic semiconductor with a band gap of 1.2 eV at room temperature and becomes ferromagnetic below Curie temperature T_c 69 K. The bottom line is that, EuO related materials are ideal compounds for both fundamental and applied spintronic research.

The general object of this research work is to synthesize and to study the morphological characteristics of Europium Oxide thin films, deposited by spray pyrolysis in aqueous and non-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 for 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 Oxide (EuO) 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), electrodeposition 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 characterization of the deposited samples was undertaken.

II. EXPERIMENTAL

A. Optimization of Parameters

The film deposition by spray pyrolysis is carried out at the optimized parameters. The spray rate, substrate temperature, concentration of spraying solution, Eu:O ratio parameters are optimized.

Spray rate: During the deposition process, it was maintained 4 psi. It is one of the important parameters in the thin film deposition. It is varied by changing the pressure on carrier gas.

Substrate temperature: To optimize the substrate temperature, the mixed equimolar precursor of europium dioxide Eu_2O_3 (99.9% pure) dissolved in dilute HCl (0.1 M), with Eu:O 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 EuO film thickness with substrate temperature was studied. It is observed that the EuO film at 573 K has maximum thickness. The decrease in thickness below 573 K may be due to complete thermal decomposition. The EuO thin films were 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 Eu. The spray rate was maintained at 3 ml/min. Plot of variation of EuO 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:O 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:O 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:O 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 EuO film deposition. Spray pyrolysis is a simple technique in which no high quality substrates are required.

III. DEPOSITION OF EUO THIN FILMS

Thin films of europium oxide (EuO) were deposited onto glass substrates from an aqueous and non-aqueous precursor bath containing europium dioxide Eu_2O_3 (99.9% pure) dissolved in dilute HCl (0.1 M), a desired molarity precursor was obtained by adding appropriate amount of double distilled water and methanol in separate beakers.

The Eu_2O_3 aqueous solution was well stirred with electrical magnetic stirrer equipment at the rate 600 rpm for 50 min. The synthesized films were of brown colored.

Each precursor was prepared in deionised water and methanol in separate beakers in equal stoichiometric volume proportions 1:1. Europium dioxide Eu_2O_3 and HCl were used as a source of Eu and O to form EuO thin films. The aqueous solution was well stirred by employing magnetic stirrer equipment at the rate 550 rpm for 45 min.

TABLE I. SYNTHESIZED EUO THIN FILM SAMPLES

SAMPLES	Deposition Parameters		
	Precursor Medium	Normality Eu_2O_3 M	Substrate Temperature K
I	Aqueous	0.01	(a) 548, (b) 573, (c) 598, (d) 623
J		0.05	
K	Non-aqueous (Methanol)	0.01	(a) 373, (b) 398, (c) 423, (d) 448
L		0.05	

IV. CHARACTERIZATIONS OF EUO THIN FILMS

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 EuO 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.

XRD pattern of EuO film samples: 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 $\text{K}\alpha$ radiation (wavelength $\lambda=0.1542$ nm). X-ray diffraction patterns recorded for the spray deposited EuO films. X-ray diffraction (XRD) is used for two reasons, one for information about crystallographic 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. The XRD pattern for aqueous and non-aqueous precursor mediums are as shown in following Figures I and II respectively.

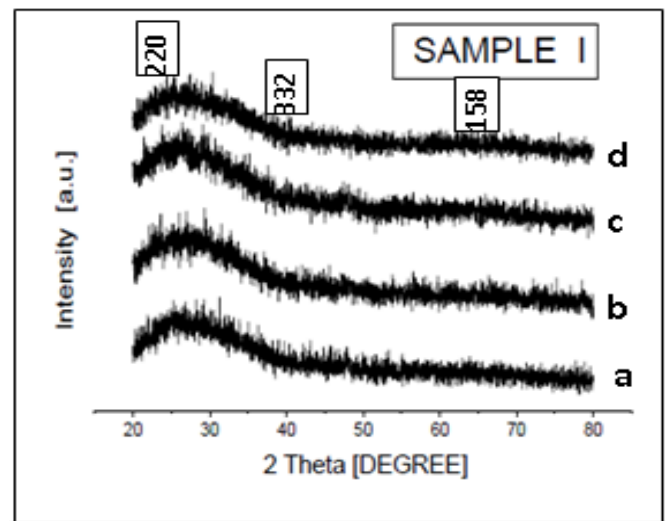


FIGURE I. THE XRD PATTERN OF EUO THIN FILM IN AQUEOUS MEDIUM

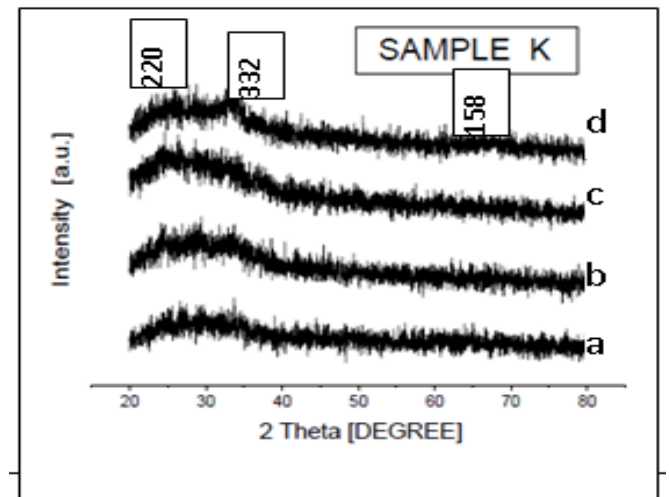


FIGURE II. THE XRD PATTERN OF EUO THIN FILM IN NON-AQUEOUS MEDIUM

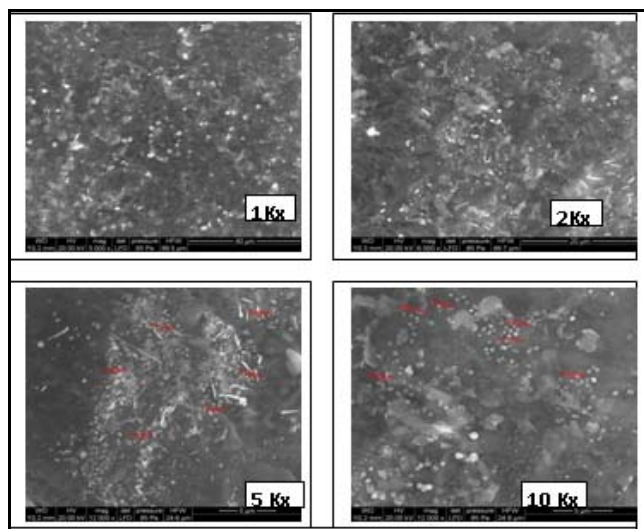


FIGURE III. THE XRD PATTERN OF EUO THIN FILM IN NON-AQUEOUS MEDIUM

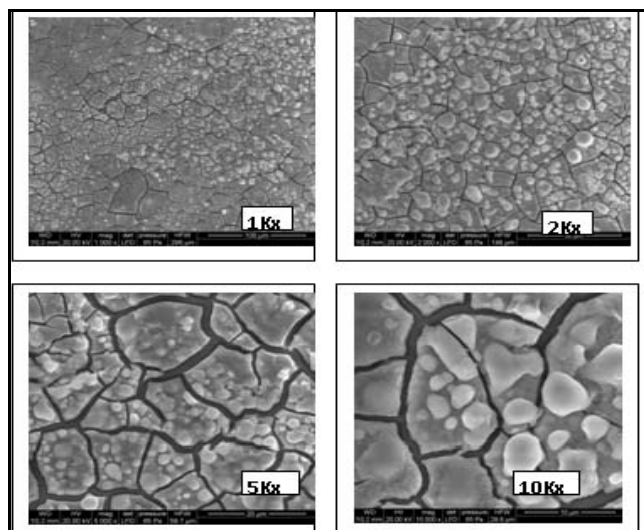


FIGURE IV. THE XRD PATTERN OF EUO THIN FILM IN NON-AQUEOUS MEDIUM

V. RESULTS AND DISCUSSIONS

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 22.340, 37.960 and 62.000 corresponding to hkl planes (220), (332) and (158) are recorded. Different 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.76-0154. The optimum temperature for deposition of good quality EuO 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 confirms that, the deposition temperature 573 K, lead to the formation of well crystallized thin films.

The broadening of the peaks at (220) reflection was used to estimate the average grain size of EuO. The grain size was estimated. The average grain size of the EuO films was found between 16 to 35 nm. The grain size of EuO was controlled by precursor concentration.

The height of (220) peak in X-ray diffraction pattern for EuO thin films deposited at temperature 573 K has observed sharper and FWHM data resulted in the enhancement of crystallite size in the deposited films at temperature 573 K. The increase in peak intensity may be attributed to increase in film crystallinity.

The crystallinity of the films is found to be increased with increasing substrate temperature from 548 K to 623 K. The average sizes of the grains are found to be 16.18 μm , which confirm the formation of well-crystallized EuO films. It shows that, at optimized parameters, EuO film has highly crystallized. It is also observed from Figure 6.5 that, the films deposited above substrate temperature 623 K are found to have maximum value of crystallite size. The decrease in thickness below the substrate temperature 573 K may be due to incomplete decomposition of precursor elements and increase in thickness above the substrate temperature 573 K may be due to complete decomposition of precursor elements.

From the micrographs one can see the uniform distribution of grain 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 Figures III and IV shows SEM images of EuO film samples I, and K respectively. It confirms the deposition of Eu and O. The elemental analysis was also carried out for Eu and O. It confirms the deposition of Eu and O. The elemental analysis was carried out for sample I.

It is observed that, the metal stoichiometry of the EuO thin films synthesized by present technique is nearly identical to the stoichiometry of the starting elements.

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