Effect of precursor medium on morphological and optical characterization of spray deposited EuO thin films

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Abstract
Europium chalcogenide (EuO) thin films have been deposited by spray pyrolysis technique on non-conductive bare soda lime glass substrates in aqueous and non-aqueous precursor mediums. The films synthesized are characterised by XRD, SEM, EDAX and UV-Visible spectrometry. The effect of precursor medium on morphological and optical properties has been investigated. The XRD studies reveal that, the films are polycrystalline in nature and the deposited material was europium oxide. It was found that, morphological and optical properties are strongly related to the precursor medium. The SEM analysis conformed the formation of small spherical and square shaped grains on overall substrate.

Keywords
EuO; precursor medium; band gap; EDAX; XRD; spray pyrolysis

1. Introduction
One of the europium chalcogenides in particular europium monoxide (EuO) is a fascinating compound having ferromagnetic semiconducting property. It is a divalent material but its compounds can occur in divalent and also in trivalent form of configurations. The europium chalcogenide materials initiate a simple crystal and magnetic structure and those are fit for their research studies. The ferromagnetic property has been found in some divalent europium compounds [1,2]. The europium chalcogenide series exhibits a simple rocksalt structure. Out of those the oxides, sulphides, and selenides are of ferromagnetic nature. The magnetic and electronic properties of europium chalcogenides Eu₅, EuO and Eu₅Se have been studied with more attention. Moreover the EuO is a model compound for a whole class of compounds with novel properties [3-5]. To the best of our knowledge, there is no report available on europium chalcogenides thin films by spray pyrolysis deposition technique. The morphological and optical properties of europium monoxide (EuO) by spray deposition have not reported so far. A number of methods of thin film deposition such as electro-deposition, vacuum evaporation, chemical bath deposition, chemical vapour deposition, spray pyrolysis etc are employed [6].

These techniques have major influence on morphological, structural and optical properties of synthesized thin films [7]. The surface morphology of the films varies with the precursor concentrations, volume ratio also with film deposition time [8-9].

In the present work, europium monoxide (EuO) thin films are deposited by spray pyrolysis method in aqueous and non-aqueous precursor mediums. Spray pyrolysis is a non vacuum, simple and low cost technique, having large area coating capacity and can be optimised for a wide control on morphological and optical properties of thin films. The synthesized films are characterised by X-ray diffraction (XRD), UV-Visible spectrometry, SEM and EDAX analysis. The results of morphological and optical characterisation are outlined.
2. Experimental

The europium chalcogenide (EuO) thin films are deposited onto non conductive bare soda lime glass substrates. The europium monoxide $\text{Eu}_2\text{O}_3$ was dissolved in 1 M hydrochloric acid. For aqueous precursor medium deionised water was employed and for non-aqueous medium methanol was employed. Aqueous and non-aqueous solutions of $\text{Eu}_2\text{O}_3$ at 0.05 M was used as a source of EuO. Magnetic stirrer was used to stir the precursors at the rate 550 rpm for 40 min. The experimental substrates were cleaned with 0.5 M hydrochloric acid and also with standard laboratory detergent Labonate. Substrates were ultrasonically cleaned with double distilled hot water for 10 min and dried well with hot air hand drier before deposition process. The film deposition for aqueous precursor medium was carried out at temperatures 523, 548, 573, 598 and 623 K and that of for non-aqueous medium was carried out at 423, 443, 463 and 483 K. The deposition was carried out on spray pyrolysis equipment (Model No. Holmark HO-TH-04). All other deposition parameters; pressure on carrier air (30 psi), substrate to spray nozzle distance (17 cm), spray duration (2 min) and precursor quantity (2 ml/min) were kept constant throughout the experiment. The carrier gas was air. The chemicals used were of analytical reagent grade (of 99% purity).

3. Results and Discussion

3.1. Structural and morphological characteristics

The structural characterization of EuO thin films was carried out on X-ray diffractometer model MiniFlex 2, with Cu $/ 30 \text{kV/15 mA and } k_\lambda$ radiation (wavelength $\lambda = 0.1542 \text{nm}$). The XRD patterns for the spray deposited EuO films on bare soda lime non conductive glass substrates for aqueous and non-aqueous precursor mediums are envisaged in following figures 1 and 2, respectively.

In figure 1, the XRD patterns are shown at temperatures (a) 523, (b) 548 and (c) 573 K also that of in figure 2 are that of at (a) 423, (b) 443 and (c) 463 K.

![Figure 1 XRD Pattern for aqueous medium](image1)
![Figure 2 XRD Pattern for non-aqueous medium](image2)

The XRD different peaks in the diffractogram were listed and the corresponding values of interplanar spacing $d$ were calculated. The $d$ values are compared with the standard one.[10] The diffraction peaks of EuO films for aqueous precursor medium are originated at 2$\theta$ values of 27.980,
35.280 and 53.160 corresponding to the hkl planes (222), (411) and (026) respectively. The diffraction peaks of EuO films for non-aqueous precursor medium are originated at 2θ values of 22.340, 37.960 and 62.000 corresponding to the hkl planes (220), (332) and (158) respectively. The XRD peaks in figures 1 and 2 indicate well crystallized EuO thin films. It conforms the polycrystalline nature and are of simple cubic structure. The optimized temperature for deposition of good quality EuO thin films for aqueous precursor medium is found as 550 K and that of for non-aqueous medium is 423 K. The height of peak in X-ray diffraction pattern at (222) plane deposited in aqueous precursor medium is found more sharper and FWHM data conforms the improvement of crystallite at temperature 523 K and that of for non-aqueous medium at (220) plane is found at temperature 445 K.

X-ray diffraction patterns of EuO thin films for aqueous and non-aqueous mediums are evaluated using FWHM data and Debye-Scherrer formula for the calculation of the crystallite size. Figure 3 displays the variation of film thickness with deposition temperature for aqueous precursor medium and figure 4 displays the variation that of for non-aqueous precursor medium. The thickness of thin films (t) was calculated by weight difference method, by using formula,

\[ t = \frac{m}{A \rho} \]

where m is the mass, A is the area and \( \rho \) is the density of the material in bulk form.

It is observed from figure 2 and 3 that, for aqueous precursor medium the film thickness increases with substrate temperature upto 550 K and that of for non-aqueous precursor medium increases upto 450 K. After the substrate temperatures 550 K and 450 K the film thickness starts to decrease in aqueous and non-aqueous precursor mediums respectively.

Figures 5 and 6 shows SEM images of EuO thin films deposited for aqueous and non-aqueous precursor mediums respectively.
Thin films are analysed on Electron Microscope SEM Model: Quanta 200 ESEM System, manufactured by Icon Analytical Equipment Pvt. Ltd, Mumbai. Figure 5 is the 12000X magnified micrograph of thin films for aqueous precursor medium, indicates the uniform film deposition and continuous coverage of the substrate surface with small spherical nanoparticles. Figure 6 is the 10000X magnified micrograph of thin films for non-aqueous precursor medium, indicates the uniform film deposition and continuous coverage of the substrate surface but with squared shaped nanoparticles. The microgram study reveals the effect of precursor medium on morphology of thin films. As a result the change in precursor medium from aqueous to non-aqueous changes the shapes of nanoparticles from spherical to square, films grow by spray pyrolysis technique of experimental precursor leads to a perfect flat surface of the films.[12-13]

The figure 7 and 8 displays the EDAX pattern of synthesized EuO thin films deposited for aqueous and non-aqueous precursor mediums respectively.

The pattern covers the peaks of Eu and O with varying intensity. The undefined peaks are assigned to the glass substrate. This conforms the deposition of Eu and O. The study reveals that the
doping percentage of europium increases in non-aqueous precursor medium as compared with aqueous precursor medium.

The elemental composition for aqueous precursor medium was analysed for Eu with weight 66.24% at 17.12% and that of for O was wt. 25.62% at 82.88%. The net intensities for Eu and O was 20.54 and 25.62 respectively, as shown in following table 1.

| ELEMENT | Wt % | At % | K ratio | Net Int. |
|---------|------|------|---------|----------|
| Eu      | 66.24| 17.12| 0.5868  | 20.54    |
| O       | 25.62| 82.88| 0.1334  | 25.62    |

Table 1. The elemental compositions of Eu and O for aqueous precursor medium.

The elemental composition for non-aqueous precursor medium was analysed for Eu with weight 76.15% at 25.16% and that of for O was wt. 23.85% at 74.84%. The net intensities for Eu and O was 24.54 and 16.96 respectively, as shown in following table 2.

| ELEMENT | Wt % | At % | K ratio | Net Int. |
|---------|------|------|---------|----------|
| Eu      | 76.15| 25.16| 69.59   | 24.54    |
| O       | 23.85| 74.84| 0.0878  | 16.96    |

Table 2. The elemental compositions of Eu and O for non-aqueous precursor medium.

3.2. Optical characterisation

The position of the absorption coefficient edge is accessed for the band gap energy calculation from the optical transmittance measurements of the EuO thin films. The absorption coefficient $\alpha$ was calculated by using the following equation,

$$\alpha = \frac{A}{\text{hv}} (\text{hv} - \text{Eg})^{1/2}$$

Where, $A$ is a slope of curve,

$\text{Eg}$ is band gap energy.

Figures 9 and 10 shows, Tauc’s plot between, the calculated values of the absorption coefficients $(\text{ahv})^2$ and hv, where hv is the photon energy and $\alpha$ is the optical absorption coefficient of the material.

**Figure 9** Plot of $(\text{ahv})^2$ versus energy hv for aqueous precursor medium

**Figure 10** Plot of $(\text{ahv})^2$ versus energy hv for non-aqueous precursor medium
The band gap energy value of the EuO films deposited for aqueous precursor medium, is calculated by extrapolating of the plots to the X-axis. Figure 9 shows a plot for the optical band gap energy for aqueous precursor medium, deposited at (A) 523 K, (B) 548 K, (C) 573 K and (D) 598 K, the energy band gap are found as 3.6, 3.7, 3.75 and 3.8 eV respectively and figure 10 shows that of for non-aqueous precursor medium, deposited at (A) 423 K, (B) 443 K and (C) 483 K, and the band gap energies are found as 3.6, 3.75, and 3.8 eV respectively. It is found that, the precursor medium have no major influence on band gap energy of thin films. The band gap value are in concord with the value reported. [11]

4. Conclusion
Spray pyrolysis technique was successfully employed to deposit europium monoxide (EuO) thin films on non-conducting bare soda lime glass substrates for aqueous and non-aqueous precursor mediums. The XRD study of the films conforms the cubic structure. Structural parameters like crystallite size, thickness are calculated and are found increased in non-aqueous precursor medium with conforming the formation of well-crystallized EuO films. The crystallinity of the thin films found increased in non-aqueous medium. Optical transmittance measurements revels that the change in precursor medium have no major influence on optical band gap energy. The optimized EuO thin film has highly crystallized.

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 recognised, Physics Research Centre, Mahatma Gandhi College, Ahmedpur, Dist. Latur, MS, India, for providing research facility for spray deposition and characterizations.

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