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Synthesis and XRD Study of Strontium Chalcogenide Thin Films Deposited on FTO Covered Glass Substrate

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ABSTRACT

Strontium Sulfide thin film was deposited on FTO coated glass surface. These films were characterized by polarization study, XRD study and SEM.

Keywords: SrS, Electrodeposition, SEM, XRD.

INTRODUCTION

The Electrodeposition technique has become very popular in recent decades, especially for thin film deposition, due to its low cost since no expensive and sophisticated vacuum equipments are required, ease of handling and ease of application to many compounds such as sulphides [1,2] and selenides which include SrS, ZnS, CdS, PbS, CdSe, CuS2, ZnSe, Sb2S3, TlS and HgS [3-12]. Strontium sulphide (SrS) is the alkaline earth metals, may be regarded as the divalent counter parts of the alkali halides, the IA-VIIB compounds. Most of the compounds of both of these groups have the same cubic crystal structure [13] and all are made up of ions having closed-shell electronic configurations similar to those of rare gases.

Among the numerous IIA-VIA compounds, strontium sulfide (SrS) is often chosen due to their high luminescent yields. In thin film form, these materials offer great potential for applications such as infrared sensors and X-ray radiation imaging plates [14],

optical storage media [15], and electroluminescent (EL) displays [16,17]. The strontium sulfide (SrS) is often chosen due to its large bandgap   (Eg > 4ev), which indicates self-absorption. In the present work, SrS films were deposited using d.c. eletrodeposition technique was used to study different parameters of (SrCl$_2$+Na$_2$S$_2$O$_3$) thin films.

METHODOLOGY

Here we have used the F : SnO$_2$ (F.T.O.) covered glass substrates of size 5 x 1.5 x 0.1 cm^3. The F: SnO$_2$ (FTO) covered glass substrate was prepared in the following manner:

Solution Preparation:
The initial ingredients used to prepare SrS thin films were as follows –
(i)   A.R. grade strontium chloride (SrCl$_2$. 6 H$_2$O)
(ii)   A.R. grade ethylenediamine tetra-acetic acid (disodium salt)
(iii)   A.R. grade hydrochloric acid (HCl)
(iv)   A.R. grade HNO$_3$
(v)   A.R. grade Sodium Thiosulphate (Na$_2$S$_2$O$_3$)
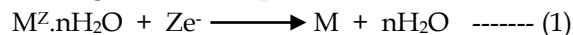
A appropriate weight of strontium chloride (SrCl$_2$.6H$_2$O) powder was taken using digital micro balance so as to get the required concentration of the solution (0.1M). The weighed strontium chloride powder was dissolved in an appropriate quantity of double distilled water to obtain desired concentration of the solution (0.1M). This solution was taken as a starting solution in electrolyte bath. The complexant Na$_2$-EDTA was prepared in double distilled water to obtain 0.1M concentration.

The strontium sulphide solution was prepared in following way. The strontium has higher reduction potential –3.122 V vs SCE [18]. This potential was reduced by complexing the strontium ion by varying the concentration of Na$_2$-EDTA with strontium chloride solution so as to form good, adherent thin films. [19, 20]. The pH = 4 was measured of the strontium chloride solution. The pH of solution was maintained constant by just simple adding dilute HCl to the strontium chloride solution. Now this solution was mixed with 0.1M Na$_2$S$_2$O$_3$ solution with appropriate ratio so as to form good quality of strontium sulphide thin films.
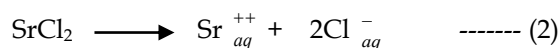
Formation of SrS Thin Film:
A general reaction in cathodic electrodeposition involving M^z ions in aqueous solution takes the form,
$$M^Z.nH_2O + Ze^- \longrightarrow M + nH_2O \quad \text{------- (1)}$$
It proceeds in following successive steps:
We have prepared firstly strontium hydroxide thin film cathodically on to the cleaned FTO glass substrate using (0.1 M SrCl$_2$.6H$_2$O+0.1M EDTA) solution in aqueous medium. The dilute HCl is mixed to these solutions to reduce the electrodeposition potential.

The chemical reduction reaction at the cathode in an aqueous solution (pH, 4) is as follows –
$$SrCl_2 \longrightarrow Sr^{++}_{aq} + 2Cl^-_{aq} \quad \text{------- (2)}$$
The decomposition of water in hydrogen and oxygen occurs according to following reaction,
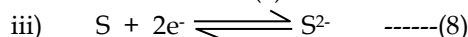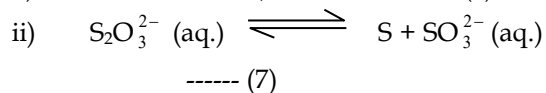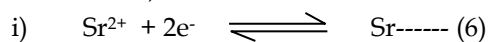$$2H_2O + 2e^- \longrightarrow 2 H^+ + 2OH - 1.0697 \text{ Vs SCE} \text{ --- (3)}$$
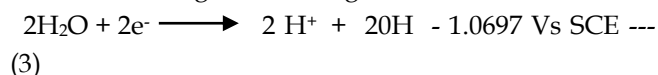
Formation of OH$^-$ ions results into changing the local pH at the cathode and there is large probability of hydroxide formation. **[21]**, as in present case the Sr(OH)$_2$ according to –
$$Sr^{2+} + 2OH^- \longrightarrow Sr(OH)_2, pH > 5 \text{ -------- (4)}$$
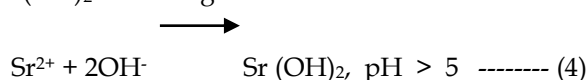
Measured pH before and after reaction was pH = 4. Thus from this mechanism it is concluded that electrodeposition from SrCl$_2$ precursor solutions onto stainless steel leads to the formation of Sr(OH)$_2$ film. Similarly sulphur film is electrodeposited from 0.1M Na$_2$S$_2$O$_3$ solution in aqueous medium (pH = 6) is as follows.
$$S_2O_3^{2-} (aq.) \rightleftharpoons S + SO_3^{2-} (aq.) \text{ ----0.75V vs SCE} \text{ ---(5)}$$
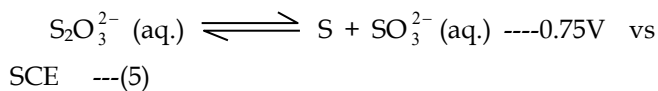
For the formation of SrS thin film, these two solutions of 0.1M normality are mixed with appropriate ratio to form a coherent, adhesive thin film. The chemical reactions for these are,
$$\text{i)} \quad Sr^{2+} + 2e^- \rightleftharpoons Sr \text{------ (6)}$$
$$\text{ii)} \quad S_2O_3^{2-} (aq.) \rightleftharpoons S + SO_3^{2-} (aq.) \text{ ------ (7)}$$
$$\text{iii)} \quad S + 2e^- \rightleftharpoons S^{2-} \text{ ------(8)}$$

iv) $Sr^{2+} + S^{2-} \longrightarrow SrS$ - - 1.0 V vs SCE ------(9)
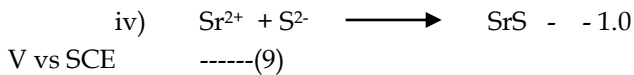
The pH value remains same before and after reaction (pH, 4). Thus we get SrS thin film, which is uniform, dense and adherent to the substrate.

RESULTS AND DISCUSSION

1) Polarization studies:

The polarization curves were drawn for the variation in current density with the potential. The deposition potentials are determined for strontium, sulphur, strontium sulphide, strontium hydroxide thin films for 0.1M concentration on FTO covered glass substrate. For strontium sulphide thin films, a whitish colour film is observed. For the potential (-1.5 V vs SCE), a strontium hydroxide thin film is formed. This potential is achieved by adding complexing agent (Na₂-EDTA) and nature of the substrates. The deposition potentials were estimated by extrapolating straight line curve portions to x-axis.

2) X-ray diffraction (XRD):

The structural identification and determination of lattice parameters are based on the interpretation of X-ray diffraction patterns. The phenomenon of X-ray diffraction can be considered as a reflection of X-rays from the crystallographic planes of the material and it is governed by Bragg's Law,
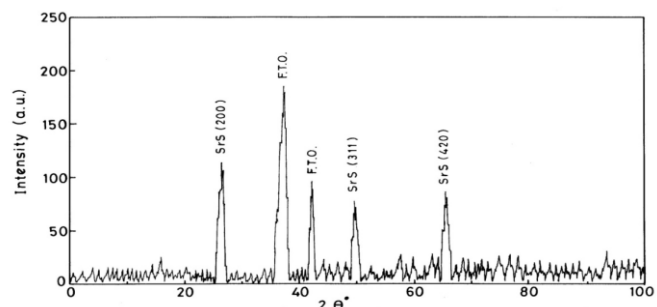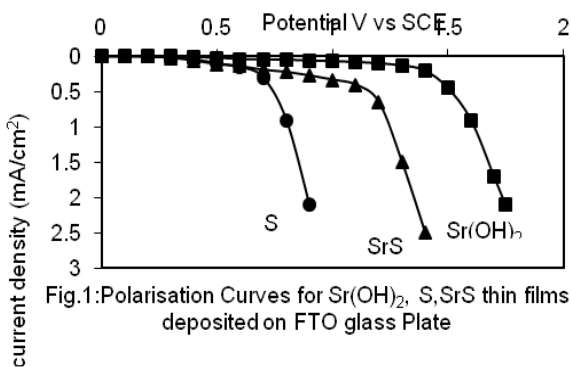
$2d Sin\theta = n\lambda$ ------ (1)

Where 'd' is the lattice spacing, λ is the wavelength of monochromatic X-rays, n is the order of diffraction (n = 1), and θ is the diffraction angle. For thin films, the powder technique (Debye-Scherrer method) [22, 23] in conjunction with diffractometer is most commonly used. The 'd' values are calculated using relation (1) for known values of θ, λ and n. For this purpose a catalogue of d-spacing of many thousands of crystals has been prepared. Joint Committee Powder Diffraction Standards (JCPDS) data of 'd' spacing is compared with the data obtained from diffractometer to identify the unknown material. This data can also be used to determine the dimensions of the unit cell.

Table 1: Electro-Deposition potentials for Sr(OH)₂, S & SrS thin films on FTO Glass Substrate.

Sr. No.	Bath Composition	Estimated Deposition Potential V vs SCE	Standard Deposition Potential V vs SCE
1	0.1 M SrCl₂ – EDTA	- 1.5	- 3.122
2	0.1 M Na₂S₂O₃	- 0.74	- 0.7182
3	0.1 M SrCl₂ – 0.1 M Na₂S₂O₃– 0.1 M EDTA – dil. HCl	- 1.2	--

Table 2 : Comparison of interplaner distance 'd' of strontium sulphide deposited on FTO coated glass substrate.

Sr. No.	Angle 2θ⁰	Observed 'd' values A⁰	Standard 'd' values A⁰	Plane h k l	Composition	Structure
1	27.432	3.0153	3.0039	(2 0 0)	SrS	Face-centered cubic
2	50.211	1.8089	1.81142	(3 1 1)	SrS	Face-centered cubic
3	67.648	1.3438	1.34338	(4 2 0)	SrS	Face-centered cubic

Fig.1:Polarisation Curves for Sr(OH)₂, S,SrS thin films deposited on FTO glass Plate

Fig. 2 : XRD Pattern of SrS Thin Film deposited on FTO Glass Substrate

From the data obtained from analyzing the sample by X-ray diffractometer, the crystallinity of the sample can be probed. From the position of reflections, the lattice parameter is calculated and using Debey-Scherrer formula the size of the crystallites (mean crystalline diameter, D) is calculated using the following relation.

$$D = 0.9\lambda \ / \ \beta \cos \theta \qquad \text{------ (2)}$$

Where λ is wavelength of X-rays, β is the full width at half maximum (FWHM) (in radians) of the peak intensity and θ is the Bragg's angle of X-ray diffraction. The X-ray diffractometer (Philips Pw - 1710) with Cukα radiation ($\lambda = 1.5418A^0$) was used for structural studies. The structural properties of strontium sulphide, films deposited on FTO coated glass substrate are studied by X-ray diffraction technique in the range of 2θ between 0^0 to 100^0. The XRD patterns of the strontium sulphide film at room temperature deposited from aqueous bath are shown in Fig. 2. The X-ray diffraction pattern of the deposited strontium sulphide film shows formation of SrS phase.

The films were polycrystalline orientation along (2 0 0). (3 1 1) and (4 2 0) plane. This plane corresponds to face centered cubic strontium sulphide. The d-values (inter planers spacing) of XRD reflection are compared with standard d-values taken from Joint Committee on Powder Diffraction Standards (JCPDS) data file for SrS, (No – 75-895), are shown in Table No. 2.
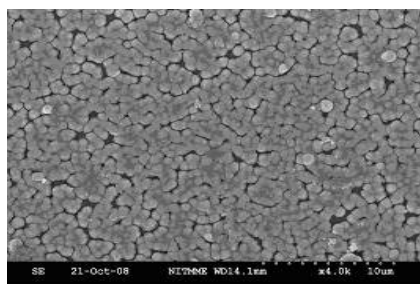
3) SEM:

Fig.3: SEM Image

Scanning electron microscopy (SEM) is a convenient method for studying the microstructure of thin films. Figure.3 show the surface morphology of SrS nanoparticle thin films deposited at room temperature and annealed at 100°C. From the micrographs, it is observed that the films were formed from uniformly deposited nanoparticles and covered the substrate well. SEM image also reveals the grain boundaries around the crystallites.

Conflicts of interest: The authors stated that no conflicts of interest.

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