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Synthesis, Structural and Morphological Analysis of SILAR Synthesized CdSe Thin Films

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ABSTRACT

Present investigation describes synthesis of CdSe thin films on stainless steel (SS) substrate from an aqueous medium. In order to prepare the best photoactive material, various synthesis parameters such as cationic precursor concentration, pH of cationic precursor solution, numbers of deposition cycles have been optimized using photoelectrochemical (PEC) procedure. The deposited films found reddish brown in color. These films were further characterized by various characterization techniques. Structure studies conducted by means of XRD and Raman spectroscopy techniques. Morphological study carried out using field emission scanning electron microscopy. The elemental composition of CdSe is certified using energy dispersive X-ray spectroscopy technique. CdSe thin films found photoactive in nature.
Keywords: *Cadmium selenide, Photoelectrochemical, Structural analysis, Morphology, SILAR*

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INTRODUCTION

The task of material synthesis in thin film form has turned out as a point of interest, because of several applications of thin film. Right from micro-electronic devices like laptop, mobile, solar cells, sensors, polarizes, anticorrosive surfaces, self-cleaning surfaces up to medical and space applications, not a single field has left untouched by thin films [1]. Numerous methods and techniques have been invented and used by the researchers, for synthesis of material in thin film form.Chemical bath deposition (CBD) is one of the attractive, cheap and simple methods [2]. The process of thin film synthesis via CBD method progresses, subsequent to exceeding of ionic product to the solubility product, consequent to precipitate formation. This precipitate formation process is necessary up to some extent for deposition of material, but it causes needless wastage of material, which cannot be prohibited. With the intention to avoid this wastage, CBD method is transformed as modified-CBD (M-CBD). M- CBD method is also called as successive ionic layer adsorption and reaction (SILAR), which is based on a fundamental surface phenomenon known as adsorption. In SILAR method, various synthesis parameters as pH, concentration, reaction and rinsing time etc. influence growth phenomenon of thin film [3, 4]. Numerous chalcogenide thin films have been synthesized by researchers via SILAR method [5]. Because of simplicity in deposition procedure and paramount benefits, SILAR method is selected, for thin film synthesis purpose.

The potency of proficient solar cell is photoelectrode material, so proper selection of it is a vital thing. The primary requisite while choosing photoelectrode material is energy band gap value, which must likely to be positioned in the vicinity of to visible spectrum maxima to make use of the solar spectrum expertly. From this perspective, II-VI binary semiconductors have been a centre point for the reasons that direct band gap, sharp absorption edges and superior absorption coefficient [6]. Cadmium selenide (band gap energy =1.7 eV) is one of the II-VI group semiconductors which has captivated interest of many researchers as a consequence of its fascinating properties and numerous applications [7-9]. Literature survey underlines, synthesis of CdSe thin films using SILAR method [10-13]. On the other hand no report is observed in the literature on synthesis and photoelectrochemical (PEC) studies of CdSe thin films on stainless steel substrate. In the present investigation, synthesis and characterization of CdSe thin films on SS substrate using SILAR method have been discussed.

MATERIAL AND METHODS

Chemicals and fabrication of PEC unit

Ever since substrate cleaning is essential in the material synthesis process to deposit good quality samples. Therefore, prior to synthesis, SS substrates (50mm×10mm×0.5mm) were polished, cleaned by way of liquor detergent, and etched in 5% H_2SO_4 for 10 minutes followed by ultrasonic cleaning.

All the chemicals utilized were of AR grade and used with no additional refinement. For synthesis of undopedCdSe thin films, both cationic and anionic precursor solutions were prepared in aqueous medium. Cadmium chloride ($CdCl_2.H_2O$) was used for supply of cadmium ions. Newly ready sodium selenosulfate (Na_2SeSO_3) solution was used as selenium ion source. Cadmium cations were complexed using tartaric acid $(CHOHCOOH)_2$. With the reason to get more photoactive material, a PEC method is preferred for parameters optimization purpose. PEC method is associated with checking of photosensitivity of samples (Jsc and Voc) in order to prefer superior photosensitive sample **[14].** With this intention, the PEC unit was made ready using two electrode configurations, among CdSe as a photoelectrode, graphite as a counter electrode and 1M polysulfide (1M NaOH- 1M Na_2S- 1M S) as a redox electrolyte.

The PEC cell performance was tested by maintaining $1cm^2$photoanode area for exposure and under illumination intensity $50mW/cm^2$. A PEC solar cell was prepared in sealed structure just through dipping the photoanode into polysulfide electrolyte.

Thin film synthesis using SILAR method and Finalization of synthesis parameters by PEC method

Experimental Setup

SILAR method contains cyclical dipping of substrate in separately placed cation and anion precursors in solution form and washing between each one dip in pure water, to avert precipitation [15]. The CdSe material possess one cationic (Cd^{+2}) and one anionic (Se^{-2}) element. Thus thin film of CdSe can be synthesized from an arrangement with 4 beaker system containing individual cationic, anionic precursor beakers and two beakers of double distilled water kept alternatively as shown in Figure 1. The experimental unit contains (A) cationic precursor bath (Cd^{+2} ion source) (B) and (D) double distilled water, (C) anionic precursor bath (Se^{-2} ion source) along with substrate holder with four substrates.

Figure1 (a) depicts, the schematic of experimental unit while (b) shows photograph of substrate holder along with substrates. The film thickness factor in SILAR method is controlled by various synthesis parameters [11]. Thus in order to grow film of optimum thickness, various preparative parameters was finalized using PEC method.

Finalization of precursor concentration

Firstly, the concentration of cadmium source was optimized. Cadmium precursor concentration was varied viz 0.1, 0.2, 0.3 and 0.4M, keeping selenium precursor concentration constant to 0.1M. The volumetric proportion of cationic and anionic precursor solutions was 1:1 maintained. For these concentration combinations, thin films were deposited retaining conditions as: pH of cationic precursor-2, pH of anionic precursor - 9, adsorption and reaction time maintained =40 s, rinsing time = 20 s and number of deposition cycles =165±5. Rate of deposition slows down corresponding to precursor concentration combination 1:1, which may be due to a lesser accessibility of solvated ions. While for precursor concentration combination 2:1, deposition of film with optimum thickness and reddish-brown color is observed. For precursor concentration combinations 3:1 and 4:1, rate of reaction initially increases rapidly and then again decreases rapidly. It may be due to speedy occurrence of precipitation process. The recorded values of Jsc and Voc were plotted as a function of cadmium ion concentration. **Figure 2 (a)** depicts variations of Jsc and Voc as a function of cadmium concentration at fixed selenium concentration. It is noticed that, values of Jsc and Voc increase with increase in cadmium concentration and attain maximum at 0.2M cadmium concentration, consequent to Cd:Se precursor concentration ratio 2:1. For further increase in cadmium precursor concentration again the PEC performance drops, may be due to stiochiometric deviation.

Optimization of cationic precursor solution pH

pH of bath controls growth rate. Tartaric acid was used for this purpose. Optimization of bath pH was carried out, by varying it from 2.8 to 1.2 (± 0.1) by an interval of 0.4.Thus depositions were carried out by maintaining optimized precursor concentrations. Appropriate amounts of tartaric acid solute were added to the cationic precursor solution so as to maintain pH at 2.8, 2.4, 2, 1.6 and 1.2(± 0.1). The recorded values of Jsc and Voc were plotted as a function of pH.**Figure 2 (b)** shows variations in Jsc and Voc as a function of cationic precursor bath pH. It is noticed that values of photosensitivity increases with decrease in bath pH (from 2.8), which reach to highest value at 2.4. For further decrease in bath pH from 2 to 1.2, both Jsc and Voc curves decline. Decrease in PEC performance at lower bath pH is attributed to powdery nature of deposited films. The powdery nature of film increases for pH values 2, 1.6, and 1.2 and also lower bath pH corrodes the stainless steel substrate. Adherent and good quality films are deposited

corresponding to cationic precursor bath pH value equal to 2.4. Thus the same is continued for further SILAR depositions.

Optimization of count of immersion cycles:

In SILAR method, the film thickness factor is mainly governed by number of immersion cycles. Thus optimization of deposition cycle number is important. Films were synthesized for different number of SILAR cycles by maintaining optimized cationic and anionic precursor concentrations and their pH values. The count of SILAR immersion cycles was varied as 125, 150, 175 and 200. PEC study of these films was carried out. Figure 2 (c) depicts the variations in photosensitivity as a function of number of SILAR immersion cycles. With increase in number of cycles, PEC response improves. The values of Jsc and Voc reach to upper limit corresponding to number of SILAR deposition cycles 175. For further increase in SILAR cycles, PEC performance drops. This can be explained as; ideally just one layer of material gets deposited on substrate per SILAR cycle. As SILAR deposition cycles continue, further layers are getting deposited which causes increase in film thickness. Hence as number of SILAR cycles increases from 125 to 150, PEC performance increases, which can be credited to increased film thickness. Utmost PEC performance shown by film corresponding to 175 cycles is credited to optimum film thickness and well adherency of deposit. After 175 cycles film thickness decreases which is probably caused by creation of porous layer outside CdSe deposit [11]. The stress generated as a result of peeling or flaking out of film, after attainment of the optimum thickness, decreases film thickness [16]. This may be responsible for drop in behavior of Jsc and Voc plots for further increase in SILAR deposition cycles. As optimum film thickness is observed consequent to 175 SILAR cycles, the same is set for deposition purpose.

Synthesis of CdSe thin films by SILAR method was carried out using optimized synthesis parameters given in **Table.1**. Deposited films were found well adherent and reddish brown in color.

Characterizations

The structural study of the films was carried out by using Philips X-ray diffractometer PW- 3710. The 2θ was varied between range 10^0 to 100^0. Morphological and compositional studies were carried out using FESEM (S-4700, Hitachi).

RESULTS AND DISCUSSION

X-ray diffraction (XRD) studies

The XRD pattern of CdSe thin film on SS substrate is shown in Figure 3. The observed XRD pattern matches well with standard JCPDS data card no. 00-019-0191 confirming the formation of CdSe with cubic crystal structure. The peaks designated by symbol * corresponds to contribution of stainless steel substrate.

The diffraction pattern for CdSe thin film contains four diffraction peaks close to 2θ values 25.27^0, 43.16^0, 50.32^0 and 82.02^0, which are indexed as (111), (220), (311) and (511) planes confirming formation of cubic phase which are in good agreement with earlier reports [17, 18].

Morphological and compositional studies The FE-SEM images of undopedCdSe thin film at two different magnifications as 10kX and 50kX are shown in Figure 4.

CdSe sample shows irregularly shaped crystallites connected such way that they imitate cauliflower-like morphology. The lower and higher magnification FE-SEM images of CdSe sample are shown in Figure 4 (a) and (a') respectively. Tsai et.al [19] reported similar kind of morphology for CZTS thin films deposited by pulsed electrodeposition method. The composition of CdSe was studied using EDAX. The EDAX pattern for the same are shown in Figure 5. The essentials of atomic proportion analysis for CdSe sample is provided in Table 2. It confirms presence of constituents in CdSe thin film. It is noticed that CdSe sample are slightly cadmium rich.

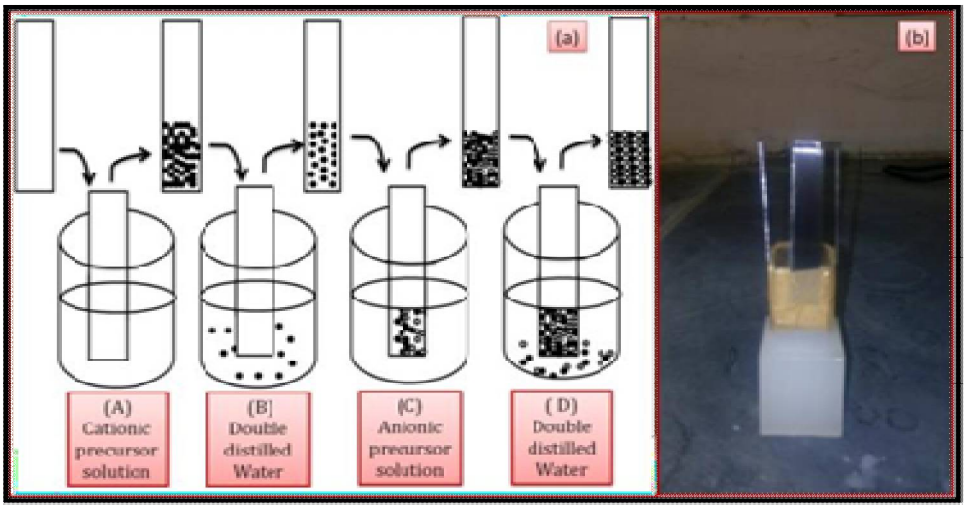

Figure 1: (a) Schematic of experimental unit used for SILAR method (b) Photo- graph of substrate holder with substrates.

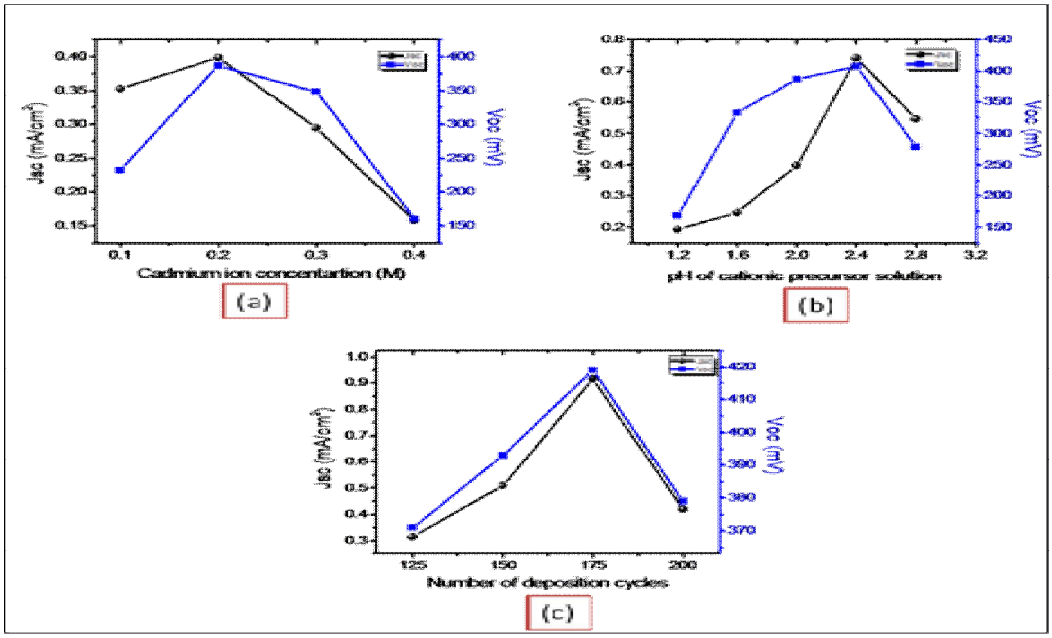

Figure 2: (a) Variations of Jsc and Voc with cadmium precursor concentration for CdSe /1M Polysulfide/Graphite PEC unit.

(a) variation of Jsc and Voc as a function of pH. (b) Variation of Jsc and Voc as a function of pH of cationic precursor solution (c) Variations of Jsc and Voc as a function of count of deposition cycles.

Table1: Optimized preparative parameters for synthesis of CdSe thin films using SILAR method.

Parameter	Details
Cationic precursor concentration	0.2MCdSO4
Anionic precursor concentration	0.1M Na2SeSO3
Complexing Agent	Tartaric acid
pH of cationic precursor bath	2.4 (± 0.1)
Adsorption and Reaction time (s)	40
Rinsing time (s)	20
Number of deposition cycles	175

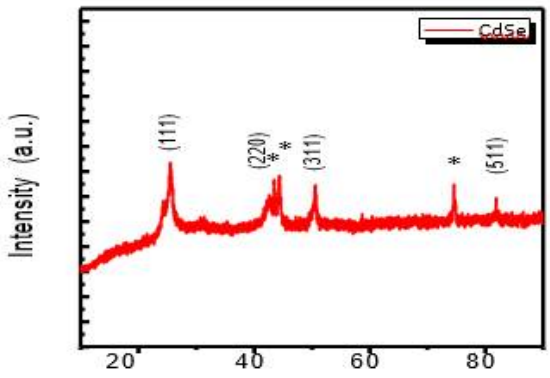

Figure3: XRD pattern of CdSe thin film Vertical lines at bottom show peaks of a cubic phase of CdSe identified by standard JCPDS card no 00-019-0191.

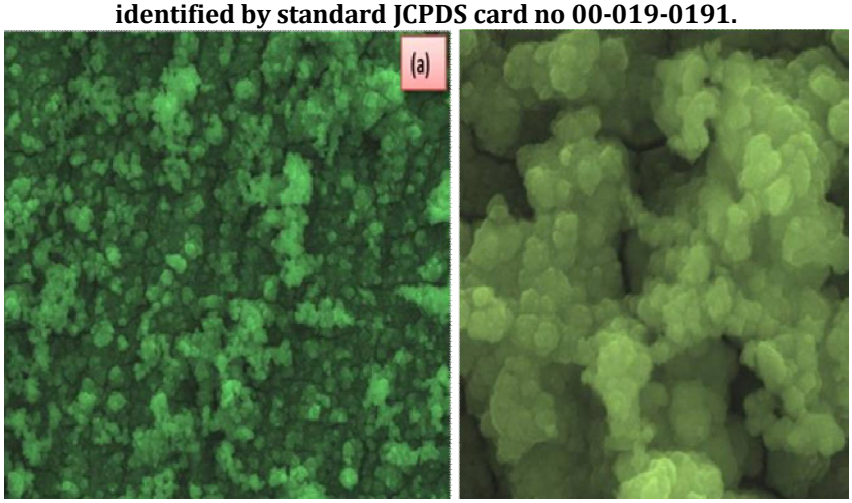

Figure 4: FESEM images of CdSe thin film (a) and (a') at 10KX and 50KX magnifications respectively.

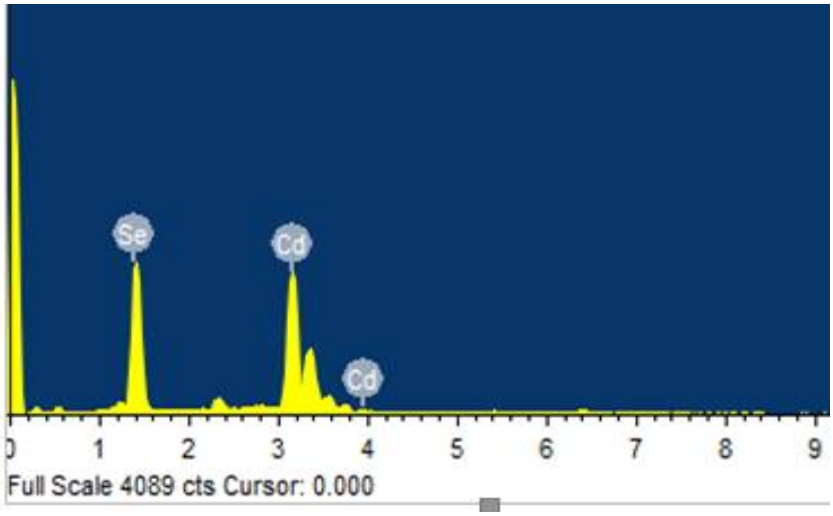

Figure 5 : EDAX pattern of CdSe sample

Table 2 : Elemental composition of CdSe sample

Sample	Atomic proportion of the constituent elements	
	Cadmium	Selenium
CdSe	52.76	47. 24

CONCLUSION

CdSe thin films have been successfully synthesized using easy and low cost SILAR method. The various optimized preparative parameters using PEC method are: concentration of cadmium precursor: 0.2M,

concentration of selenium precursor: 0.1M, bath pH: 2.4, and deposition cycles: 175. Structural study confirmed cubic crystal structure of the deposit. The CdSe thin film exhibits cauliflower-like morphology. EDAX analysis validated deposition of CdSe thin film. CdSe thin film found photoactive in nature.

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