Materials Science and Engineering B 174 (2010) 242–248

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

# Electrodeposition and characterization of Fe doped CdSe thin films from aqueous solution

S. Thanikaikarasan[a,*], K. Sundaram[a], T. Mahalingam[a,*], S. Velumani[b], Jin-Koo Rhee[c]

[a] Department of Physics, Alagappa University, Karaikudi-630 003, India
[b] Centro de Investigación y de Estudios Avanzados del I.P.N.(CINVESTAV),Av. Instituto Politécnico,Nacional 2508,Col. San Pedro Zacatenco, 07360, México D.F
[c] Millimeter-wave Innovation Technology Research Center, Dongguk University, Seoul- 100 715, Korea

ARTICLE INFO

*Article history:*
Received 27 August 2009
Received in revised form 17 March 2010
Accepted 19 March 2010

*Keywords:*
Cadmium selenide
thin films
doping effects
optical properties
strain
dislocation density
photoelectrochemical solar cells

ABSTRACT

Thin films of Cadmium selenide (CdSe) and Ferrous (Fe) doped Cadmium selenide (CdSe:Fe) have been deposited on indium doped tin oxide coated conducting glass (ITO) substrates using potentiostatic electrodeposition technique.The mechanism of formation of CdSe and CdSe:Fe have been analyzed in the potential range between −1500 and +1500 mV versus SCE. X-ray diffraction pattern reveals that the deposited films possess hexagonal structure with preferential orientation along (002) plane. The dependency of microstructural parameters such as crystallite size, strain and dislocation density with $FeSO_4$ concentration for CdSe:Fe thin films are studied. Surface morphology and film composition shows that films with smooth surface and well defined stoichiometry is obtained at 0.01 M dopant ($FeSO_4$) concentration. Optical parameters such as band gap, refractive index and extinction coefficient for CdSe and CdSe:Fe thin films are estimated using optical absorption measurements. Photoelectrochemical solar cells are constructed using CdSe and CdSe:Fe as photocathode in 1 M each of $Na_2S$, S and NaOH as redox electrolyte and their power output characteristics are studied.



## 1. Introduction

Binary semiconductors of II-VI group attracts many researchers, because of their wide range of applications in solid state devices, such as solar cells, opto-electronic devices, solar selective coatings [1–3]. Among II-VI group semiconductors, CdSe is an important material which has been mainly utilized for photoelectrochemical solar cells and opto-electronic devices [1]. CdSe is found to be an excellent material with a direct band gap value of 1.7 eV which make them interesting for photoelectrochemical solar cells, because of their compatibility of its bandgap with the solar spectrum [4,5]. Thin films of CdSe are usually crystallized in both cubic (zinc blende) structure(JCPDS-ICDD 2003, 19-0191) with lattice constant (a = 6.077 Å) and in hexagonal (wurtzite) structure (JCPDS-ICDD 2003, 08-0459) with lattice constants (a = 4.299 Å; c = 7.010 Å). Numerous methods have been used to obtain CdSe thin films with both cubic and hexagonal structures: (i) vacuum evaporation [6], (ii) pulsed laser deposition (PLD) [7], chemical solution deposition [8]. In many of the semiconductor devices, the formation of low resistance, metal-based, ohmic contacts requires the establishment of a heavily doped region directly beneath the metal contact. If the surface layer is doped sufficiently high, the current flow across the interface proceeds principally through tunneling at the fermi level. The resistivity of polycrystalline material mainly depends upon the grain boundary or surface scattering effects [9]. The photoelectrodes based on CdSe have been observed to be susceptible to electrochemical corrosion [10]. In order to get low resistance contact, it is essential to obtain CdSe films which are doped with a suitable donor impurity concentration, the resistivity of the photoelectrode material could be reduced. Recently, much attention has been given to tailor the optical and electrical properties of these materials by using suitable dopants such as Zn, Fe and Sb [7,10,11]. The process of doping different dopants which causes the broadening of intra gap impurity bands and the formation of band tails and band gap renormalization [7]. The process of doping transition metals with CdSe find numerous applications in visible region [10]. The presence of VIII group element (such as Fe) as a dopant material with CdSe exhibit considerable effect in the number of host lattices [10]. Masumdar et al reported the growth mechanism, crystallographic, microscopic observations, optical and electrical properties of Sb doped thin films prepared using solution growth process [11]. The structural, electrical, optical and Raman spectroscopic measurements of Zn

* Corresponding author at: Department of Physics, Alagappa University, Karaikudi-630 003, India. Tel.: +91 04565 230 251/82 31 219 1847; fax: +82 31 212 9531.
*E-mail addresses:* S_thanikai@rediffmail.com (S. Thanikaikarasan), maha51@rediffmail.com (T. Mahalingam).

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doi:10.1016/j.mseb.2010.03.054

doped CdSe thin films obtained using pulsed laser deposition technique has been reported earlier by Perna et al. [7]. Among the above mentioned deposition techniques, electrodeposition provide numerous advantages over vacuum and other processes, such as low temperature growth, control of film thickness and morphology, potentially low capital cost. One obvious requirement is that the substrate must be conductive [12,16]. Pawar et al have prepared Fe doped CdSe (CdSe:Fe) thin films from non-aqueous electrolytic bath using electrodeposition technique [10]. There is no such report available for studying the effect of dopant concentration in electrodeposited CdSe:Fe thin films from aqueous electrolytic bath. Hence, an attempt is made to study the dopant concentration effect in electrodeposited CdSe:Fe thin films.

In this work, we have reported our results on the preparation and characterization of CdSe and CdSe:Fe thin films obtained from an aqueous electrolytic bath consists of $CdSO_4$, $SeO_2$, $FeSO_4$ and triethanolamine. The deposition mechanism has been investigated using cyclic voltammetry. Structural properties of the deposited films are analyzed using X-ray diffraction. Microstructural parameters such as crystallite size, strain and dislocation density are evaluated for CdSe:Fe thin films. Also, the morphological, compositional, optical and photoelectrochemical properties of CdSe and CdSe:Fe thin films are studied. The effect of dopant ($FeSO_4$) concentration on the above properties of the films are studied. The experimental observations are discussed in detail.

## 2. Experimental details

The chemicals used in this work were of Analar Grade reagents. CdSe thin films were deposited on indium doped tin oxide coated conducting glass (ITO) substrates from an aqueous electrolytic bath consists of 0.01 M $CdSO_4$, 0.01 M $SeO_2$. By adding adjustable amount of dilute sulphuric acid the pH of the electrolytic bath was adjusted to $2.5 \pm 0.1$. At lower pH value, such as below $2.5 \pm 0.1$ adherence of the film to the substrate was very poor. At higher pH value such as above $2.5 \pm 0.1$, there is precipitation of $CdSO_4$ occurs which yields films with poor quality. Hence, an optimum solution pH value of $2.5 \pm 0.1$ must be fixed in order to get good quality films. The electrochemical experiments were carried out using a PAR scanning potentiostat/galvanostat unit (Model 362, EG & G, Princeton Applied Research, USA) employing three electrode configuration with ITO substrate as cathode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode, respectively. Before used for deposition, ITO substrates were treated for 15 minutes with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The SCE was introduced into the solution by luggin capillary whose tip was placed as close as possible to the working electrode. Fe doped CdSe films (CdSe:Fe) was obtained by using 0.01 M $FeSO_4$ solution added in the deposition bath during the process of deposition of CdSe thin films. To obtain stoichiometric films with Fe doping, it is essential to reduce the deposition rate of Fe when compared to CdSe. This could be obtained by adding 0.005 M triethanolmine (TEA) as complexing agent with $FeSO_4$ solution. This mixture was added in an aqueous acidic bath containing $CdSO_4$ and $SeO_2$ in order to obtain CdSe:Fe films. The concentration of iron triethanolamine mixture was so adjusted, such that the formation of other compounds of Fe and Se were inhibited. The deposition potential was fixed as −700 mV versus SCE for CdSe and CdSe:Fe thin films using cyclic voltammetry. The films deposited at lower bath temperature such as below 80 °C were poorly crystallized, whereas the films deposited at higher bath temperature such as above 80 °C, the current densities were found to be higher. These higher current densities increase the rate of deposition which in turn causes peel of the film from the substrate. Hence, the bath temperature was fixed as 80 °C for CdSe and CdSe:Fe thin films. The optimum deposition conditions used for the preparation of CdSe and CdSe:Fe thin films were: Solution pH: $2.5 \pm 0.1$, Bath temperature:80 °C, Deposition potential:-700 mV versus SCE.

Cyclic voltammetric studies was taken out in a standard three compartment cell using BAS 200A electrochemical analyzer. Thickness of CdSe and CdSe:Fe films was estimated using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer (XPERT PRO PANalytical, Netherland) with $CuK_\alpha$ radiation ($\lambda = 1.540$ Å) was used to identify the crystalline nature and phases of the deposited films. The surface morphology and film composition were analyzed using an energy dispersive analysis by X-rays set up attached with scanning electron microscope (JEOL JSM 840). Optical absorption spectrum of the samples was recorded using an UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics, USA). Photoelectrochemical measurements of CdSe and CdSe:Fe thin films was carried out using three electrode system comprising of CdSe and CdSe:Fe thin film as photocathode, platinum electrode as counter electrode and SCE as reference electrode, respectively.

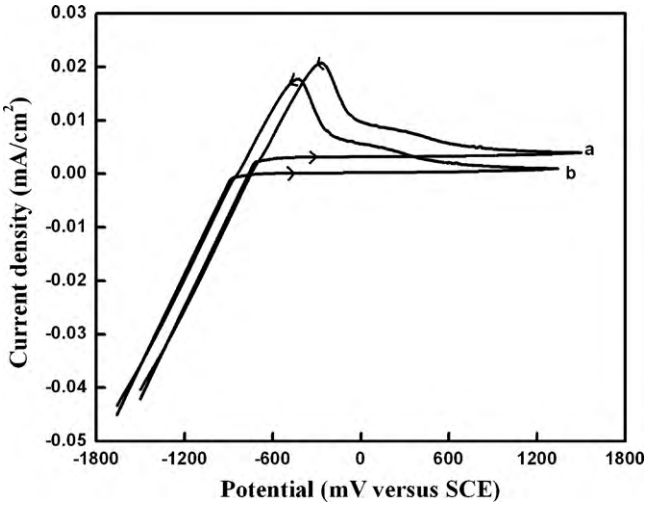


**Fig. 1.** Cyclic voltammogram of ITO glass electrode: (a) Electrolyte solution mixture containing 0.01 M $CdSO_4$ and 0.01 M $SeO_2$. (b) Electrolyte solution mixture containing 0.01 M $CdSO_4$, 0.01 M $FeSO_4$,0.01 M $SeO_2$ and 0.005 M TEA.

## 3. Results and Discussion

### 3.1. Cyclic voltammetric studies

Cyclic voltammetry is a powerful analytical tool for studying electrochemical reaction in solutions of $CdSO_4$, $SeO_2$ and $FeSO_4$. Cyclic voltammetric studies was performed in a standard three electrode cell consists of ITO substrate as cathode, platinum electrode as anode and SCE as reference electrode, respectively. The scan rate employed was 20 mV/sec. The voltammetric curves were scanned in the potential range from −1500 to +1500 mV versus SCE. Fig. 1a shows the typical cyclic voltammogram recorded for ITO glass electrode in an aqueous solution mixture containing 0.01 M $CdSO_4$ and 0.01 M $SeO_2$. It is observed from Fig. 1a, that the growth of CdSe starts at a potential −717 mV versus SCE. During cathodic scan, the reoxidation peak observed at −600 mV versus SCE which is responsible for superimposed peaks of compound CdSe and element Cd, since this peak is similar to pure solution of $CdSO_4$ and hence no oxidation peak of CdSe is found. A hysteresis is obtained in the potential range between −717 and −699 mV versus SCE indicates that the deposition of CdSe occurs more easily on the CdSe surface than those on ITO surface, since the working electrode is initially covered with CdSe instead of ITO. Hence, the formation of CdSe starts at a more positive deposition potential on the surface of CdSe electrode [13]. The reduction of $H_2SeO_3$ to Se is the rate controlling step in the deposition process, the first is the reduction of $Cd^{2+}$ to Cd on the surface of ITO electrode which is followed by electrochemical reduction of $H_2SeO_3$ with element Cd according to the following Eq. (1).

$$Cd + H_2SeO_3 + 4H^+ + 4e^- \rightarrow CdSe + 3H_2O \quad (1)$$

Fig. 1b shows the cyclic voltammogram recorded for ITO glass electrode in an aqueous solution mixture containing 0.01 M $CdSO_4$, 0.01 M $SeO_2$, 0.01 M $FeSO_4$ and 0.005 M TEA as complexing agent. A slight shift in oxidation and reduction potential observed may be due to the addition of $FeSO_4$ and TEA in an aqueous solution mixture consists of $CdSO_4$ and $SeO_2$. The co-deposition of Fe along with CdSe which is confirmed from elemental compositional analysis.

### 3.2. Film thickness

The electrochemical growth of CdSe and CdSe:Fe thin films is controlled by two separate variables such as (i) film thickness and