



## Electronic energy levels and electrochemical properties of co-electrodeposited CdSe thin films

H. Bayramoglu, A. Peksoz\*

Physics Department, Faculty of Arts and Sciences, Uludag University, Gorukle Campus, 16059 Bursa, Turkey



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### ABSTRACT

CdSe semiconductor thin films were grown on indium tin oxide (ITO) coated glass substrates by co-electrochemical deposition method. Deposition potential was kept at  $-0.95$  V vs. Ag/AgCl reference electrode for ten minutes. Deposition electrolyte includes an aqueous solution of 10 mM CdCl<sub>2</sub>, 20 mM H<sub>2</sub>SeO<sub>3</sub> as precursors, 200 mM LiCl as complexing agent, and HCl for adjusting of pH. Deposited CdSe thin film was annealed at 500 °C for 30 min in air medium. Precursor and annealed CdSe thin films were characterized using a number of techniques, including SEM, EDX, XRD, UV–vis spectroscopy, and electrochemical impedance spectroscopy. SEM studies show that annealing alters the surface of precursor CdSe film from smooth to granular appearance. According to EDX analyses, the ratio of Cd/Se is close to 1.07 and 1.04 for the precursor and annealed CdSe thin film, respectively. XRD analysis shows that each film has polycrystalline structure. Precursor film has only cubic structure of CdSe, while annealed film has hexagonal structure of CdSe and cubic crystal phase of CdO. Optical energy band gap of the as-deposited CdSe film increases from 1.64 to 1.71 eV after annealing due to the mixture of the two phases. Refractive index against wavelength changes between 2.0 and 3.3. Calculations performed by using the data of Mott-Schottky measurements show that precursor CdSe film has  $1.72 \times 10^{16}$  cm<sup>-3</sup>, while annealed film is of  $3.65 \times 10^{17}$  cm<sup>-3</sup> carrier concentration. The prepared films exhibit n-type semiconductor character. The study reports energy level diagrams of the produced semiconductor CdSe thin films by using the Mott-Schottky and Tauc's approximations. The carrier transport properties in the interface between active CdSe thin film and electrolyte are discussed based on an equivalent electronic circuit simulated to the Nyquist data of the CdSe/electrolyte system.

### 1. Introduction

Cadmium selenide (CdSe) is a well-known II-VI semiconductor material due to its direct and narrow band gap, large absorption in the visible region and high electron affinity [1,2]. CdSe generally exhibits cubic zinc blende and hexagonal wurtzite crystal structures [2,3]. CdSe has either n-type or p-type semiconductor character. In electro-deposition technique, the conductivity type of CdSe thin film can be adjustable by controlling Cd/Se ratio. Se surplus in CdSe thin films can lead to p-type conductivity. In the past few decades, CdSe semiconductor materials have attracted a grand deal of attention because of applications in solar cells, thin film transistors, light emitting devices [4–6]. To enlarge potential use in new application areas, researchers have been trying to change physical and chemical properties of CdSe semiconductor materials by using different deposition techniques and different production conditions. CdSe thin films have been produced by physical vapor deposition [7–9], chemical vapor deposition [10,11],

thermal evaporation [12], spray-pyrolysis [13,14], dip coating [15,16], chemical bath deposition [17,18], molecular beam epitaxy [6,19], magnetron sputtering [20,21] and electrodeposition [1,3,22–25]. Among these techniques, electrodeposition is an easy and low-cost technique. By electrochemical deposition technique, large area thin films can be produced in non-vacuum medium and at room temperature conditions.

The aim of this work is to deposit easily cadmium selenide thin films by co-electrodeposition technique in a single electrolyte, and to present details of the crystalline and microstructural studies, optical and electrical properties of precursor and annealed CdSe semiconductor thin films. This paper also discusses the use of chronoamperometry technique at a constant potential to prepare good-quality films of CdSe. There are limited investigations on the Mott-Schottky studies, the determination of electronic energy band structure, and electrochemical impedance spectroscopy analyses of the electrochemically synthesized CdSe thin films. This study also reports a complete description related

\* Corresponding author. Postal address: Solar Cell Laboratory, Physics Department, Sciences and Arts Faculty, Uludag University, 16059 Gorukle, Bursa, Turkey.  
E-mail address: [peksoz@uludag.edu.tr](mailto:peksoz@uludag.edu.tr) (A. Peksoz).

with the determination of the electronic energy level diagram from the Mott-Schottky measurements and the required theoretical relations, and electrochemical properties of the deposited CdSe thin films.

## 2. Materials and methods

### 2.1. Material

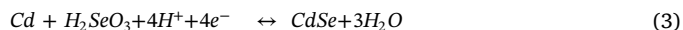
Cadmium (II) chloride ( $\text{CdCl}_2$ ), selenous acid ( $\text{H}_2\text{SeO}_3$ ), lithium chloride ( $\text{LiCl}$ ) and hydrochloric acid ( $\text{HCl}$ ) were purchased from Sigma-Aldrich. The purity of all compounds is greater than 99%. Indium tin oxide (ITO) coated glass substrate with a sheet resistance  $< 10 \Omega/\text{square}$  and  $1 \text{ cm}^2$  surface area was used as a working electrode. Prior to the film growth, the ITO surfaces were carefully cleaned with acetone and then pure water in ultrasonic cleaner. Finally, the cleaned ITO surfaces were dried in air medium to be ready for the film growth.

### 2.2. Co-electrodeposition of CdSe thin films

A Gamry Reference 3000 Potentiostat/Galvanostat was used for electrochemical production and measurements. A schematic demonstration of the electrodeposition setup was given in our early works [26,27]. The electrochemical system includes three electrodes. In this configuration, ITO-coated glass, platinum mesh and saturated  $\text{Ag}/\text{AgCl}$  are used as working electrode, counter electrode and reference electrode, respectively. Some important advantages of a three-electrode system over a two-electrode deposition system were explained in our early work [27].

In this study,  $\text{CdCl}_2$  and  $\text{H}_2\text{SeO}_3$  are used as Cd and Se sources, respectively. It is important to determine cyclic voltammogram of the Cd and Se sources and thus understand reaction mechanisms of the components in the film to be prepared. Fig. 1 shows cyclic voltammogram recorded in the aqueous electrolyte consisting 20 mM  $\text{CdCl}_2$  and 10 mM  $\text{H}_2\text{SeO}_3$ . The peak observed at  $-0.89 \text{ V}$  is attributed to the Se deposition (Fig. 1). In the forward scan, the peak observed at  $-0.87 \text{ V}$  is due to the reduction of  $\text{Cd}^{2+}$  to Cd on the surface of ITO working electrode according to Eq. (1). In the reverse scan, the intense peak at  $-0.26 \text{ V}$  is related to the dissolution of Cd (Fig. 1). The electrochemical

reactions during CdSe growth can be expressed as [28]:



Growth electrolyte consists of 10 mM  $\text{CdCl}_2$ , 20 mM  $\text{H}_2\text{SeO}_3$ , 200 mM  $\text{LiCl}$  and 50 cc pure water. For appropriate deposition conditions, it is required to decrease the electrolyte resistance to a lower level by lowering pH value. Therefore, hydrochloric acid was added to the deposition solution to adjust pH  $\sim 2.1$ . CdSe thin films were grown on ITO surfaces by co-electrodeposition in a single deposition electrolyte. Film growth was controlled by chronoamperometry method, which is available in PHY200 physiochemical package software. Deposition potential is selected as  $0.95 \text{ V}$  to avoid rapid deposition, because the deposition potential is  $-0.87$  and  $-0.89 \text{ V}$  for Cd and Se, respectively. Deposition potential was kept at  $-0.95 \text{ V}$  for ten min at room temperature. The inset in Fig. 1 shows time-current variation in the co-electrodeposition of precursor CdSe thin film for 600 s. The current-time variation can be described in three time regions in terms of deposition of CdSe thin film (the inset in Fig. 1). First region is 0–0.1 s short time period, second 0.1–33 s, and finally third is 33–600 s time interval. The current changes sharply from  $1.4 \text{ mA}$  to  $-87 \text{ mA}$  between 0 and 0.1 s. In this very short time, one-dimensional (1D) CdSe film occurs. The current decreases from  $-87 \text{ mA}$  to  $-32 \text{ mA}$  in the time interval between 0.1 s and 33 s due to the rapid deposition of CdSe, and the formation of two-dimensional (2D) CdSe happens in the second region. Three-dimensional (3D) CdSe film occurs between 33 s and 600 s. The current remains stable ( $\sim 32 \text{ mA}$ ) over the time period from 33 s to 600 s. According to the recorded data, the current starts with  $32.38 \text{ mA}$  when time is 33 s, and ends with  $31.93 \text{ mA}$  when the time is 600 s. This is because conductivity of the working electrode decreases due to the increasing in thickness of the coated CdSe film.

### 2.3. Measurements

PHY200 Physical Electrochemistry software in the Gamry Reference 3000 Potentiostat/Galvanostat/ZRA system was utilized to control chronoamperometry method at room temperature. Surface formations of the films were imaged with scanning electron microscope (SEM) by a Carl Zeiss EVO 40 system (Carl Zeiss NTS Limited Company, Cambridge, UK). Atomic components of the CdSe materials were detected by Bruker AXS Microanalysis energy dispersive X-ray (EDX) analysis processed at  $20 \text{ keV}$  with XFlash 4010 detector. The structural investigation of the films was carried out by using Bruker X-ray diffractometer D8 advance model. The source of radiation was  $\text{CuK}\alpha$  with  $\lambda_{\text{K}\alpha} = 1.54060 \text{ \AA}$ . The optical absorption and reflection spectra were recorded using a UV-vis spectrometer (Shimadzu UV-2600, Japan). Film thicknesses were measured by optical profilometer (Zeta-20, Zeta Instruments, United States).

## 3. Results and discussion

### 3.1. SEM and EDX studies

Fig. 2 shows a top view of precursor and annealed CdSe thin films. It can be considered that annealing has a strong effect on the surface nanostructure of CdSe thin films, compared Fig. 2a and b. Precursor CdSe thin film has smooth surface, as seen Fig. 2a. The whole surface of annealed CdSe thin film is seen to be uniformly covered with spheres (Fig. 2b). The size of diameters of these spheres is in the range of about  $140\text{--}900 \text{ nm}$  (Fig. 2b). EDX analysis confirms that Cd/Se ratio is 1.07 and 1.04 for precursor and annealed CdSe thin films, respectively (Fig. 3).

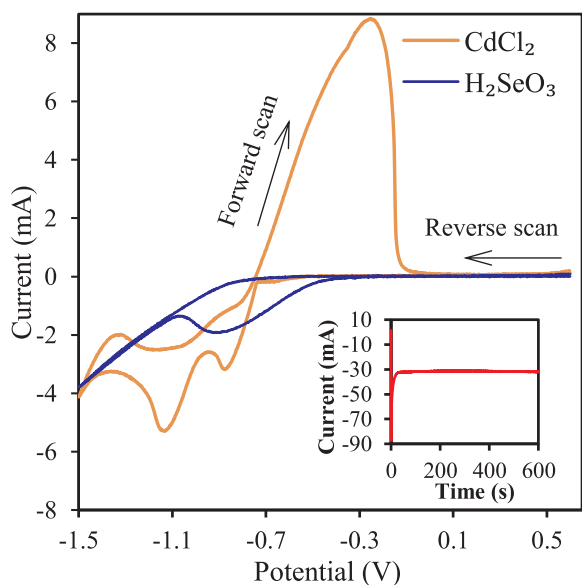


Fig. 1. Cyclic voltammograms of the aqueous 20 mM  $\text{CdCl}_2$  + 200 mM  $\text{LiCl}$  and 10 mM  $\text{H}_2\text{SeO}_3$  + 200 mM  $\text{LiCl}$  electrolytes at room temperature. The inset shows potentiostatic current-time curve recorded on ITO electrode during the electrodeposition of CdSe thin film.

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