Journal of Electroanalytical Chemistry 742 (2015) 23–29

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Structural, optical and electrical properties of electrodeposited cadmium selenide thin films for applications in photodetector and photoelectrochemical cell

S. Mahato *, A.K. Kar

Department of Applied Physics, Indian School of Mines, Dhanbad 826004, Jharkhand, India

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 30 December 2014
Accepted 27 January 2015
Available online 4 February 2015

Keywords:
CdSe thin film
Electrodeposition
Photoconductivity
Photoelectrochemical cell

ABSTRACT

Nanocrystalline cadmium selenide (CdSe) thin films have been deposited on indium tin oxide (ITO) coated glass substrates at room temperature (28 °C) by using simple two electrode electrodeposition process. The preparative parameters such as deposition time, deposition potential, concentration of solution, pH value of electrolyte have been optimized for deposition of uniform CdSe thin films. The films were annealed at 250 °C for 30 min in air and characterized using X-ray diffraction, optical absorption spectrophotometer, Scanning Electron Microscope, Current–Voltage–Temperature measurements, photoconductivity and photoelectrochemical cell (PEC) measurements. XRD studies identify that the hexagonal (Wurtzite) phase present in the deposited CdSe thin films is highly oriented to [002] direction. Optical band gap is found to decrease with increase in annealing temperature. Electrical properties exhibit that the films are semiconducting. Photoresponse of the films increases with increase of exposure time. The construction of fabricated photoelectrochemical cell is CdSe|NaOH (1 M) + S (1 M) + Na_2S (1 M)|Graphite. The cell shows that the CdSe thin films have two different zones of metallic character under both dark and illumination conditions and their conversion efficiency is 1.16%.

1. Introduction

Cadmium Selenide (CdSe) is a well known II–VI group compound semiconductor of the periodic table. The semiconductor is important and interesting because of their potential applications in photoconductor [1,2], light emitting diode [3], solar cell [4], photovoltaic cell [5] as well as photoelectrochemical cell (PEC) [6]. The material is highly photosensitive in visible region because of their suitable band gap (1.74 eV).

Different processes such as physical vapour deposition [7], chemical vapour deposition [8], spray-pyrolysis [9], chemical bath deposition [10] and electrodeposition [11] have been used for depositing cadmium selenide thin films. But the electrodeposition process is one of the simplest and low-cost techniques because it is easy to manage and needs very simple equipment. The deposition rate is easily controlled by changing the deposition potential, deposition time, concentration of solution and pH of the electrolyte; it is also used for large area thin film deposition without need of vacuum.

Investigation of photoconducting properties of CdSe thin films are of quite interest due to their application in optoelectronic devices. The photoresponse of CdSe thin film mainly consists of three parts: First is photogeneration and recombination of electron–hole [e–h] pairs by the absorption of incident light whose photon energy is greater than the band gap energy of the material in the device; second is the charge separation and transport of e–h pairs by external electric field and third is related to the surface which is a slow process attributed to the adsorption on the surface of nanoparticles [12]. In photoconductivity, the variation of photocurrent as a function of various parameters such as intensity of light, exposure time, applied field, energy of illumination, temperature and other parameters gives valuable information regarding the material [13].

A PEC directly converts solar energy into chemical energy that can be stored in molecules such as hydrogen through the electrochemical reaction. In the energy conservation process, photoanode or photocathode should have suitable band gap to absorb the solar energy spectrum for the whole visible range, and the semiconductor electrode must be stable against photoanodic or photocathodic reactions. The electrodes are immersed in a redox electrolyte solution for oxidation on one n-type semiconductor electrode and for reduction on other electrode through solar illumination. Thus the

* Corresponding author.
E-mail address: som.phy.ism@gmail.com (S. Mahato).

http://dx.doi.org/10.1016/j.jelechem.2015.01.034
1572-6657/

composition of redox electrolytic solution does not change; but the electricity is obtained as in usual solid-state solar cell. The cell construction is simple and cell has the advantage that it can be used for conversion of solar energy to both electrical energy and chemical energy [14,15]. Optimization of preparative parameters of photosensitive semiconducting electrodes by PEC method is a new, reliable and unique technique in thin film research. Photoelectrochemical cells based on semiconductor–electrolyte junctions have been attracting a great deal of interest in solar and non-solar applications, as they have many advantages over conventional solid-state junctions [16].

The aim of this present work is to prepare cadmium selenide thin films by simple two electrode electrodeposition process on ITO coated glass substrates for applications in photosensitive device and photoelectrochemical cell (PEC). The crystalline and microstructural analysis, optical absorption spectroscopy, and electrical properties of the films are being presented and discussed.

2. Experimental details

2.1. Film deposition

For deposition of CdSe thin films, cadmium chloride ($CdCl_2$) was used as a source of cadmium and selenous acid (H_2SeO_3) was used as a source of selenium in the electrolyte. Cadmium selenide thin films have been deposited onto indium tin oxide coated glass substrates by using a simple electrodeposition process. ITO, having sheet resistance 10 ohm/sq was used as a working electrode or cathode, and a graphite rod was used as an anode. Substrates were cleaned thoroughly before deposition. In the electrolyte the molar concentrations of cadmium chloride and selenous acid were 0.08 M and 0.005 M respectively [17]. The electrolyte was continuously stirred for 15 min by using a Teflon coated magnetic paddle and stirrer to perfectly dissolve the ingredients in distilled water. All the chemicals used had 99.99% purity and procured from Sigma Aldrich. The total volume of electrolyte was 100 ml and the temperature was maintained at 28 °C. pH value of the electrolyte was kept at 1.5. During electrodeposition, deposition potential was fixed at 2.20 V and deposition time was maintained for 30 min. After deposition the thin film coated ITO substrates was taken out from the electrolyte and washed with distilled water and dried in air for a few minute. The as-deposited films were next annealed at 250 °C in the air for 30 min.

2.2. Reaction mechanism

The reaction mechanism of CdSe thin film deposited on ITO coated glass substrate is discussed as follows. The deposition process is based on the slow release of Cd^{2+} ions and Se^{2-} ions in the solution ion-by-ion basis on to the ITO coated glass substrates. The deposition takes place when the ionic product of Cd^{2+} and Se^{2-} is greater than solubility product. The growth mechanism of film can be understood from the following reaction [18].

$$H_2SeO_3 + Cd^{2+} + 6e^- + 4H^+ \leftrightarrow CdSe + 3H_2O$$

In the first step: The reduction of cadmium chloride to cadmium ions occurs in the solution.

$$CdCl_2 \leftrightarrow Cd^{2+} + 2Cl^-$$

In the second step: The reduction of selenious acid into selenium oxianion occurs in the solution. Reactions are shown below.

$$H_2SeO_3 \leftrightarrow H^+ + HSeO_3^-$$

$$HSeO_3^- \leftrightarrow H^+ + SeO_3^{2-}$$

But in slightly acidic condition the selenium oxianion (SeO_3^{2-}) is transformed into ($HSeO_3^-$) ions and for more acidic condition it forms selenious acid.

In the third step: Kazacos and Miller [19] have reported that in an acidic medium, H_2SeO_3 can reduce to elemental selenium ions through the reaction.

$$H_2SeO_3 + 4H^+ + 4e^- \leftrightarrow Se + 3H_2O$$

$$H_2SeO_3 + 6H^+ + 6e^- \leftrightarrow H_2Se + 3H_2O$$

$$H_2Se \leftrightarrow Se^{2-} + 2H^+$$

$$Cd^{2+} + Se^{2-} \leftrightarrow CdSe$$

Therefore, the simultaneous formation of CdSe and deposition of elemental selenium is possible. In fact, the relative rates of formation of CdSe and Se are decided by the bath parameters such as pH, concentration and temperature of electrolyte [20].

2.3. Film characterization

X-ray diffraction (XRD) patterns were recorded using XRD (BRUKER D8 – FOCUS) system, using Cu Kα radiation (λ = 1.5406 Å). 2θ scan was taken for the range of 10–80° with a speed of 0.20°/s and with a step size of 0.030°. Optical absorption spectra were obtained for the region 200 nm–1100 nm using UV–Vis–NIR spectrophotometer (make and model?). The emission spectra have been recorded to study photoluminescence phenomena with Hitachi Make F-2500 Fluorescence Spectrophotometer. The microstructure of the CdSe thin film was studied using a scanning electron microscope (SEM, Model: 6390LV, Jeol).

A photoelectrochemical cell was used to determine the photoconductivity of cadmium selenide thin films, as shown in Fig. 1. A freshly prepared polysulphide solution of [NaOH (1 M) + S (1 M) + Na_2S (1 M)] was used as the redox electrolyte. Deposited CdSe thin film was used as a photoanode and a graphite rod was used as a cathode; the two electrodes were externally connected with a digital voltmeter and ammeter. The distance between the photoanode and counter electrode was 1 cm. The photoanode area exposed to light was 1 × 1 cm^2 [21]. All the reagents and chemicals used were of analytical reagent (AR) grade. A 500 W tungsten filament lamp (intensity 20 mW/cm^2) was used as a light source. Lamp and detector arrangement was made on a metallic rail where PEC itself acted as a detector. *I–V* measurements were performed using a Keithley 2400 source metre. Photoconductivity was also tested outside PEC in dry condition directly over the film surface using the same source metre. The light source was a 100 W (intensity 3.5 mW/cm^2) tungsten bulb controlled by a dc power supply. The light source was placed 20 cm away from the sample.

3. Results and discussion

3.1. Crystallinity

Fig. 2 shows typical XRD patterns of as-deposited and annealed CdSe thin films on ITO coated glass substrates. Several well defined peaks are observed in the XRD pattern. It is found that CdSe films are highly oriented with hexagonal (würtzite) crystal structure. The highest intensity peak at (002) plane is much stronger than other peaks. Sharp and intense peaks signify good crystallinity of CdSe thin films and also secure the nature of the thin films. In the background a small hump can be noticed on as-deposited CdSe thin film [Fig. 2(b)]; it is due to the partial amorphous nature of ITO coated glass substrates. The hump is totally suppressed when the