

The Characteristics of the Crystal of CdSe thin films fabricated by electrochemical techniques

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Abstract: CdSe thin films, using for the optoelectronic applications such as photoconductor and solar cell, have been fabricated by the electrochemical electrodeposition techniques. The cyclic voltammograms were used to decide electrodeposition potential, and the electrodeposited CdSe thin films have been analyzed according to the photoelectrochemical experiment. The crystallinity and the surface morphology have been studied X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. From photoelectrochemical experiment, the electrodeposited CdSe thin films were grown by n-type semiconductor and flatband potential was ca. -0.4 ~ -0.46 V vs. SCE. XRD patterns were informed to be consisted of cubic crystallinity structure. SEM results showed that the sizes of grain were from 0.1 to 1.0 μm . The energy bandgaps of CdSe thin films by the cyclic and the potentiostatic electrodeposition techniques were 1.78 and 1.81 eV, respectively.

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Keywords: CdSe; thin films; XRD; SEM; flat band

1. Introduction

The group II–VI compound semiconductor such as CdSe, CdTe, ZnSe, ZnTe and Hg CdTe and so on are important in a wide spectrum of optoelectronic application ranging from photoconductor, solar cells, light-emitting diodes, biological sensors and infrared detection device[1-3]. While selenide and telluride semiconductors have considerable interest due to their important applications as laser materials, optical filters and sensors, optical recording materials, and solar cells [4-9]. Several physical and chemical techniques are available for the growth for thin films of CdSe[10-13] There are several methods for the preparation including solid-state reactions[14], electrochemical methods[15-16], microwave-assisted preparation [17-18], chemical path deposition [19-22], high-temperature pyrolysis of single source precursors[23-24], vacuum deposition[25], H₂Se methods [26-28], and photochemical methods[29]. The films of these materials hitherto have been mainly synthesized via vacuum techniques. In particular, the electrodeposition method has advantage over other processes because of its simplicity, low equipment cost and the possibility in making large area thin films. Its method occurs closer to room temperature than high temperature and affords precise process control.

In this paper, it is aimed in the present work to prepare CdSe thin films fabricated by electrochemical electrodeposition in aqueous solution. We investigate electrochemical behavior of CdSe thin films deposition from a simple aqueous solution, design to electrodeposited CdSe film and present the

results of structural, morphological and optical studies of CdSe thin films electrodeposited onto transparent conducting glass.

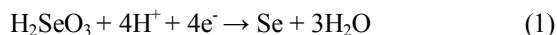
2. Experimental

A standard three electrodes configuration was employed using with ITO glass substrate as the working electrode, platinum as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode to electrodeposit CdSe thin films. All the potentials are reported versus the potential of SCE. Pt working electrode was prepared by flame cleaning and then quenched and cooled in Millipore Milli-Q water and in air, sequentially[30]. The electrolyte consisted of 20mM CdSO₄ and 1mM SeO₂ solution with an initial pH adjusted to 4mM H₂SO₄. Analytical grade reagents were used. The bath temperature was room temperature. Prior to the film deposition, the ITO substrates were cleaned with detergent and diluted hydrochloric acid and were then rinsed with distilled water. Electrodeposition[31] was carried out under cyclic and potentiostatic condition using PINE RDE4 Potentiostat/Galvanostat. The samples were annealed in air for 30 min. The surface morphology of the films was studied by JSM-6700F scanning electron microscope (SEM) operated at an accelerating voltage of 8 kV. X-ray diffraction (XRD) measurements were performed by a Philips MRD diffractometer with Cu K α radiation. Optical absorption studies were carried out employing a NKT1200 ultraviolet-visible-near infrared spectrophotometer.

3. Results and Discussion

Reaction and Photocurrent characteristics:

The electrochemically generated selenium then react chemically with Cd²⁺ ions in the solution to form at the cathode.



The overall expression of the reaction therefore is,

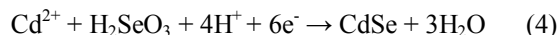


Figure 1 show the dependence of the current potential curve on incident light intensity for best cells we have constructed. As observed for CdSe the potential where photocurrent onset is observed to shift negative, with increasing light intensity. The limiting photocurrents are seen to increase linearly with light intensity up to ~ 100mW/cm² indicating that the hole population is the factor limiting the maximum photocurrents observable under these conditions. Under these conditions, electron-hole recombination dynamics start to effect the photocurrent response. the onset potential is the flatband potential extracted from Mott-Schottky data, E_{fb} = -0.4 ~ -0.46V vs SCE. Under the light intensity, heterogeneous charge transfer is controlled uniquely by the degree of band bending.

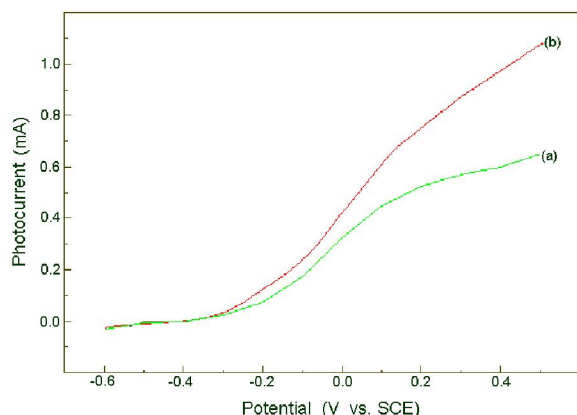


Figure 1. Comparison photocurrent with electrodeposition techniques:
(a) potentiostatic electrodeposition technique (PET)
(b) cyclic electrodeposition technique (CET)

The biased photocurrent response of the semiconductor-liquid junction has been widely used to obtain information on the flat band potential E_{fb},

minority carrier diffusion length and donor concentration. The technique is based on Butler's model which treats the semiconductor-liquid junction as an ideal Schottky barrier. The reaction kinetics and the carrier recombinations within the depletion layers as well as at the surface are ignored

XRD Studies:

XRD was used to determine the degree of crystallinity of CdSe as well as the unit cell shapes and lattice parameters. Moreover, the Debye-Scherrer equation was used to estimate the particle size of the CdSe NPs depending on the full-width at half-maximum of diffraction peaks, as the particle size increases the broadening increases. The XRD patterns of CET and PET are shown in Fig. 2(a) and (b), respectively. The CdSe has diffraction peak angles at 2θ = 25.9° and 42.7° corresponding to (1 1 1) and (2 2 0), plane reflections of cubic CdSe with cell constant a = 6.09 Å (JCPDS No. 19-191). Furthermore, the diffraction peak angle at the shoulder representing the amorphous part of the polymer was found to be increased in the case of CdSe, due to decreasing the degree of crystallinity.

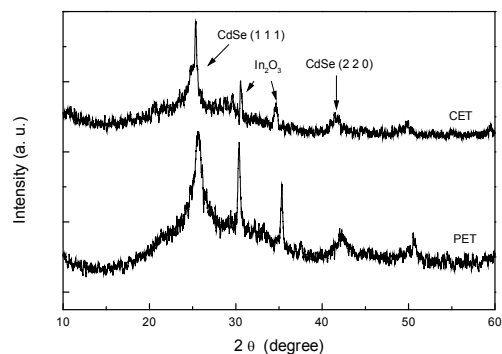


Figure 2. XRD pattern according to CET and PET

SEM Images:

Scanning electron microscopy was used to determine the effect of deposition techniques. The surface appears granular at 10,000x magnification; these grains, which range in size from 0.1 to 1 μm, are probably either aggregates of much smaller crystals of amorphous. Another film grown at PET and CET had cracks and larger grain sizes in the Fig 3.

The grain sizes of CET and PET are shown 0.5 ~ 1 μm and 0.1 ~ 0.3 μm in Fig. 3 (a) and (b), respectively. As a results, the photocurrents shown fig. 1 are related to the grain sizes

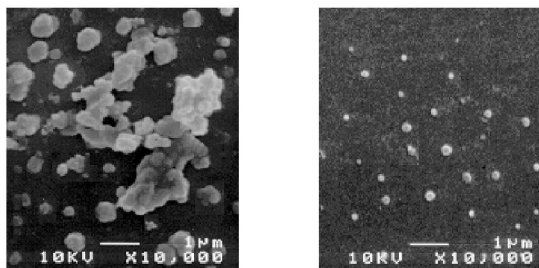
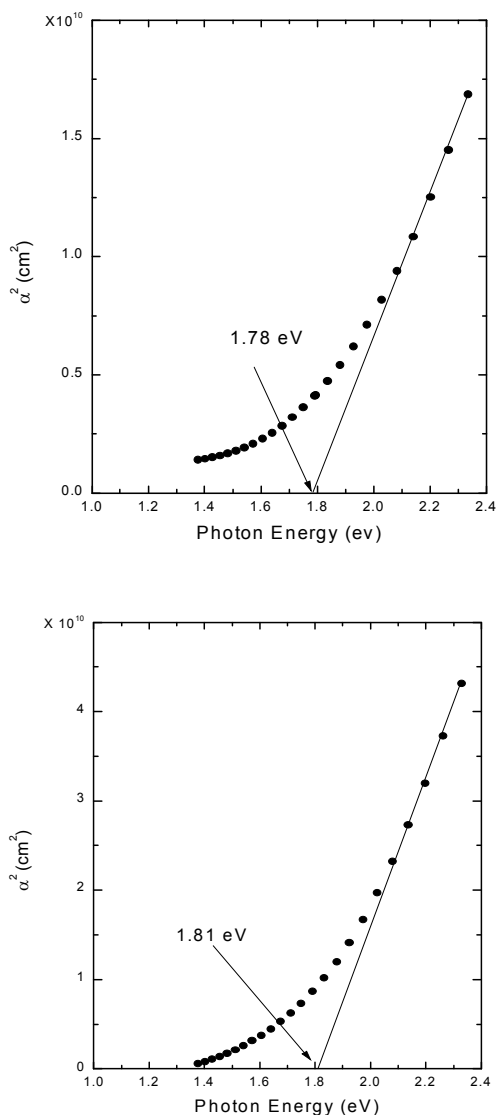


Figure 3. SEM photos: (a) CET and (b) PET

Optical properties:

Figure 4. $(\alpha hv)^2$ vs. $h\nu$ plot of CdSe films deposited at different technique: (a) CET and (b) PET

Optical absorption measurements were made at room temperature by placing an ITO conducting glass substrate in the reference beam. A plot of $(\alpha hv)^2$ versus $h\nu$ for the films deposited at different electrodeposition techniques is shown in Fig. 4. The plot is linear indicating the direct band gap nature of the films. Extrapolation of the line to the $h\nu$ axis indicated a direct band gap in the range 1.78 – 1.81 eV as the particle size is decreased. This is due to the decrease in particle size. The variation of band gap is due to the variation of crystallite size shown fig.3. The energy bandgaps of CdSe thin films by the cyclic and the potentiostatic electrodeposition techniques were 1.78 and 1.81 eV, respectively. The variation in the degree of crystallinity could be attributed to the interaction between CET CdSe and PET CdSe crystals, which were found to be inversely proportional with the particle size.

4. Conclusion

CdSe thin films using for the optoelectronic applications have been fabricated by the electrochemical electrodeposition techniques. The crystallinity, the surface morphology, the compositional ratio, and the energy bandgap have been analyzed according to the photoelectrochemical experiment, X-ray diffraction(XRD), scanning electron microscopy(SEM), and the optical absorbance, respectively. Photoelectrochemical experiment could be measured to elucidate information of the formation of CdSe thin films. Electrodeposited CdSe thin films were acted as photoanodic electrodes. It has been seen to be n-type semiconductor. Flatband potential of electrodeposited CdSe thin films was ca. $-0.4 \sim -0.46$ V vs. SCE. From the result of XRD measurement, The largest peaks were appeared from the 25.3° (1 1 1) direction and small peaks from the 42° (2 2 0) direction for electrodeposited CdSe thin film. It was manifest that electrodeposited CdSe thin film was consisted of cubic crystalline structure. SEM results showed that the sizes of grain were from $0.5\mu\text{m}$ to $1\mu\text{m}$ and from 0.1 to $0.5\mu\text{m}$ by the cyclic and the potentiostatic electrodeposition techniques, respectively. According to the surface morphology, it could be seen that the thin films had porous surface. The energy bandgaps of CdSe thin films by the cyclic and the potentiostatic electrodeposition techniques were 1.78 and 1.81 eV, respectively. The variation in the degree of crystallinity could be attributed to the interaction between CET CdSe and PET CdSe crystals, which were found to be inversely proportional with the particle size

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