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Study on electrodeposited $CdSe_xTe_{1-x}$ semiconducting thin films

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ABSTRACT

Electrochemical deposition and characterization of CdSeTe thin film has been presented in this work. $CdSe_xTe_{1-x}$ $(0<x<1)$ compound thin films have been electrodeposited cathodically on SnO_2 conducting glass slides using various pH values and deposition potentials using an electrolyte bath solution consisting of $CdSO_4$, SeO_2 and TeO_2 at different temperatures. The composition in the films has been found to vary linearly with the composition in the bath solution. The increase of selenium content 'x' in the $CdSe_xTe_{1-x}$ films has increased the band gap of the film. Photoelectrochemical solar cell studies were done and its response with concentration of Se was studied and these results have been discussed in this report.

1. Introduction

The II–VI semiconducting materials are very interesting and potential candidate for this ever-advancing technological fields, recently ternary alloys of semiconducting materials have received much attention in the fields of optoelectronic devices [1,2] and solar energy conversion [3] owing to their properties of band gap and lattice constant modulation by composition and other growth parameters. Binary and ternary chalcogenide semiconductors such as CdSe, CdTe and its alloys have received widespread interest in the field of photo-catalysis and conversion of solar energy. CdSe and CdTe semiconductors form a solid solution throughout the entire composition in the compound $CdSe_xTe_{1-x}$. $CdSe_xTe_{1-x}$ films with 'x' varying in between 0 and 1 exhibit very interesting semiconducting properties such as direct transition, not very large band gap width (1.35–1.75 eV), and short penetration length of the light. These materials can be advantageously used for various technological applications in particular for the conversion of solar energy in photoelectrochemical devices [4], and this compound can also be used for the photo-assisted decomposition of water. For best solar energy conversion, the band gap of the semiconductor should be very close to the maximum energy in the visible spectrum to utilize the solar spectrum efficiently. $CdSe_xTe_{1-x}$ is one of the best materials to tune the band gap suitable for solar energy conversion application.

$CdSe_xTe_{1-x}$ materials can easily be synthesized by numerous preparation methods in the form of thin polycrystalline films with considerable application potential. These thin films are synthesized using several sophisticated techniques, such as molecular beam epitaxy [5], electron beam evaporation [6], thermal evaporation [7], and hot wall deposition [8]. Though there are number of reports on $CdSe_xTe_{1-x}$ thin films prepared using various techniques but the works on the electrodeposition of $CdSe_xTe_{1-x}$ are scarce. In particular, electrochemical preparation techniques employing cathodic, or anodic routes from aqueous or non-aqueous electrolytes, has many advantages over other techniques. Electrodeposition [9,10] is a simple and low cost fabrication technique, has been successfully applied to obtain semiconducting materials on SnO_2 and other conductive substrates. The crystallinity can be improved significantly by careful monitoring of the electrodeposition parameters. Stoichiometry of the film can be controlled and thereby band gap tuning is possible in this technique. The aim of this work was to study the effect of bath composition on the structural, morphological and optical properties of the electrodeposited $CdSe_xTe_{1-x}$. Cathodic electrodeposition of $CdSe_xTe_{1-x}$ thin films from aqueous solutions and its study is detailed in this report.

2. Experimental details

Polycrystalline thin films of $CdSe_xTe_{1-x}$ (x = 0.2, 0.4, 0.6 and 0.8) have been deposited under potentiostatic condition. Depositions were carried out from the aqueous solutions containing 0.1–0.5 M $CdSO_4$, 0–1 mM TeO_2, and 0–2 mM SeO_2. All the chemicals used in this deposition were of analytical reagent grade (99% purity, E-Merk). Fluorine doped SnO_2 covered glass slides of 1 cm × 1.5 cm area were used as substrates (resistance 10–15 Ω/□) to electrodeposit $CdSe_xTe_{1-x}$ thin films. As the solubility of TeO_2 in water is very low, it requires several hours for its dissolution in

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water. To avoid this problem the TeO_2 was first dissolved in concentrated sulfuric acid and then diluted with water. The pH value was adjusted to 4 and the bath temperature was varied from 50 to 90 °C. A three-electrode cell arrangement system was used with a SnO_2 covered glass as substrate, a graphite sheet as counter electrode and a saturated calomel electrode (SCE) as the reference electrode for this deposition. A heater with magnetic stirrer was used to provide stirring and to keep the temperature of the bath constant. The potential was controlled using potentiostat (EG & G, Princeton Applied Research, USA, Model 362). Before deposition the substrates were cleaned with detergent, dried and degreased with acetone and distilled water. After film formation, the samples were rinsed with distilled water, dried and stored in a desiccator for further studies. The film thickness was measured using multiple beam interferometry and microbalance techniques. The deposited films were analyzed using X-ray diffraction (XRD) by Bruker Discover D8 diffractometer with Cu Kα radiation of wavelength $\lambda = 0.15418$ nm. Surface morphological and compositional analyses were carried out using a scanning electron microscope and energy dispersive X-ray analysis set-up (EDAX) attached with SEM (Philips, Model XL 30). Optical measurements were carried out using a JASCO V-570 spectrophotometer. AFM micrograph was also used to observe the surface morphology of the thin films. Photoelectrode was prepared using the as-prepared CdSeTe films; this electrode was immersed in 2.5 M HCl for 10 s and rinsed in deionized water. A photoelectrochemical (PEC) solar cell was fabricated using $CdSe_xTe_{1-x}$ films as the working electrode in a three-electrode arrangement consisting of a carbon rod and SCE as counter and reference electrodes, respectively, in 0.25 M polyiodide (NaOH–KI–I_2) electrolyte. The solar cell power characteristics were measured using 100 mW lamp.

3. Results and discussion

3.1. Growth and physical study

The electrodeposition of ternary $CdSe_xTe_{1-x}$ thin films is very similar to the case of binary compounds CdSe and CdTe. In this deposition process when a suitable potential is applied between the electrodes, the ions undergo the discharge process and the deposits of $CdSe_xTe_{1-x}$ is formed by solid-state reaction between the deposited species as

$$\mathrm{Cd} + \mathrm{Se} \Leftrightarrow \mathrm{CdSe}$$

$$\mathrm{Cd} + \mathrm{Te} \Leftrightarrow \mathrm{CdTe}$$

$$x\mathrm{CdSe} + (1-x)\,\mathrm{CdTe} \Leftrightarrow \mathrm{CdSe}_x\mathrm{Te}_{1-x}$$

The process can be systematically divided into three steps. At first, Se^{4+} and Te^{4+} are reduced to Se and Te atoms, which are absorbed on the cathodic surface that is already partially occupied by Cd^{2+} absorbed ions. In the second step, at the contact with the Se and Te adatoms, Cd^{2+} cations are reduced to give Cd^0 adatoms. Finally the $CdSe_xTe_{1-x}$ compound is formed by crystallization of Cd^0 with Se^0 and Te^0 adatoms. In order to avoid an excess of chalcogen and to get a layer composition closer to the stoichiometric ratio, it is necessary to have a large excess of Cd^{2+} ions. So that, the surface concentration of adsorbed chalcogen atoms can be reduced to increase the rate of second step process. For this purpose, the electrolyte composition and the deposition parameters have to be chosen in such a manner that the current is limited by the diffusion of Se^{4+} and Te^{4+} ions.

Numbers of deposits were produced using various growth conditions such as bath concentration, deposition potential, solution pH and temperature. The deposition potential was varied between −0.5 and −1.2 V, the potential −0.7 V was found to result in uniform good adherent films without any turbulent gas evolution during deposition. The optimum growth condition to deposit stoichiometric crystalline $CdSe_xTe_{1-x}$ film was optimized after analyzing preliminary data of the grown films. The optimum condition identified as suitable for the growth of quality $CdSe_xTe_{1-x}$ thin films was deposition potential −0.7 V versus SCE, solution pH 4, bath temperature 80 °C and electrolyte concentration 0.5 M $CdSO_4$, 0.5 mM TeO_2, and 1 mM SeO_2. Temperature of the electrolyte solution plays an important role in the mechanism of electrodeposition and in the quality of the film. The bath temperature is expected to influence the deposition rate by increasing the diffusion coefficient of the species and precursor solubility. The films deposited at a temperature below 60 °C were found to be poorly crystallized and amorphous in nature. For the temperatures above 60 °C, the films were found to exhibit well-defined X-ray diffraction peaks corresponding to the alloy. The deposition rate was found vary linearly with time, temperature and precursor concentrations in the deposition bath. Films deposited at pH 4 have yielded significant results. For pH below 2.5, excessive amount of pure Te was deposited while at pH greater than 4 Se excessive films were obtained. The films were found to have Cd excess at the potentials less than −1.0 V. In case of precursor concentration, the change of $CdSO_4$ concentration in the electrolyte solution has not shown any change in the XRD peaks. The composition of Se in the film was found to increase with the SeO_2 concentration of the bath. Fig. 1 shows the variation of Se composition in the film for the change in bath concentration of SeO_2. The increase of Se concentration has been found to saturate after 1.2 mM of SeO_2. For the solution concentration of SeO_2 above 1 mM, selenium excess films were obtained.

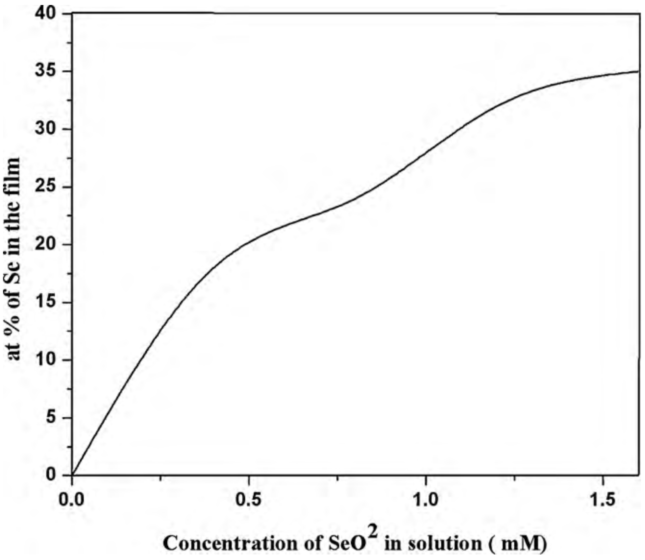

Fig. 1. Variation of Se in the film with SeO_2 concentration in the solution bath.

3.2. Structural characterization

Structural properties such as crystallinity, surface morphology, particle shape and size of the grown films were analyzed using XRD full-width half-maximum (FWHM) and SEM techniques. Fig. 2 shows XRD pattern of the electrodeposited $CdSe_xTe_{1-x}$ film with film composition $x = 0.58$. The presence of sharp peaks reveals that the grown films are polycrystalline in nature. The peaks of XRD pattern exhibit hexagonal wurtzite structure with preferred orientation along (0 0 2), (1 0 2), (1 1 0), (2 0 1) and (2 1 0) directions.

The lattice parameter values of the films have been determined and it has been given in Table 1. These values are in good agreement with the values reported by earlier workers [11]. The lattice

Table 1
Comparison of calculated *d* values with standard *d* values of CdSeTe.

S. no.	Calculated d_{hkl} (Å)	Standard d_{hkl} (Å)	*h k l*
1	7.075	7.089	0 0 2
2	3.956	3.967	1 0 2
3	2.584	2.593	1 1 0
4	2.256	2.246	2 0 1
5	1.748	1.743	2 1 0

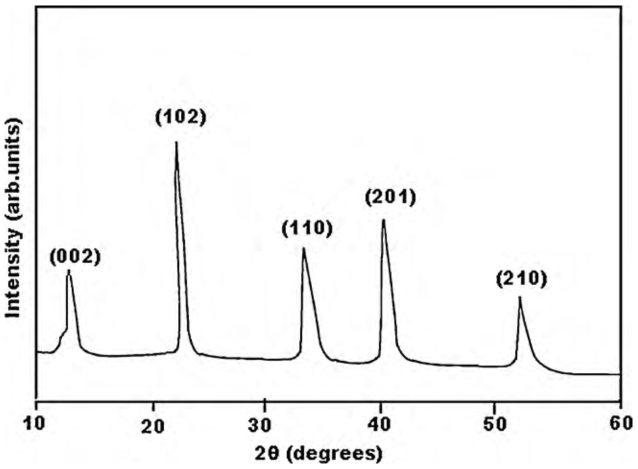

Fig. 2. X-ray diffraction pattern of $CdSe_{0.62}Te_{0.38}$ thin film.

parameter values of the films have been determined as $a = 4.342$ Å, $c = 7.265$ for (1 0 2) plane. The crystallite size was estimated from XRD pattern using Scherrer equation:

$$\text{Size} = \frac{0.9\lambda}{\text{FWHM} - \cos\theta}$$

where λ is the wavelength of the X-ray and θ is the diffraction angle for (1 0 2) plane. The average crystallite size of the film was found as approximately 200 nm.

Surface topography of the layers has been investigated by scanning electron microscopy and atomic force microscopy. Fig. 3 shows the scanning electron micrograph of as-grown $CdSe_xTe_{1-x}$ thin film with $x = 0.58$. It has homogeneous smooth surface with grains in spherical shape. The grains have a round shape with different sizes ranging from 150 to 200 nm. Atomic force microscopic (AFM) measurements were taken from small 10 μm × 10 μm samples cleaved from substrate's edge. Fig. 4 represents three dimensional (3D) atomic force micrographs of $CdSe_xTe_{1-x}$ films electrodeposited in optimized condition. AFM images can be used to measure the Z range, root mean square (RMS) roughness, grain size, and surface morphology of the prepared films. The Z range is the height difference between the lowest and highest features on the sample. RMS roughness represents the standard deviation between the height of topographic features and the mean feature height. Grain size is determined by the stereological techniques. This method cannot give actual grain size but describes the diameter of distinctive granular surface features, which may or may not reflect actual grain size. It showed rough surface with grains of different sizes covering the whole substrate uniformly.

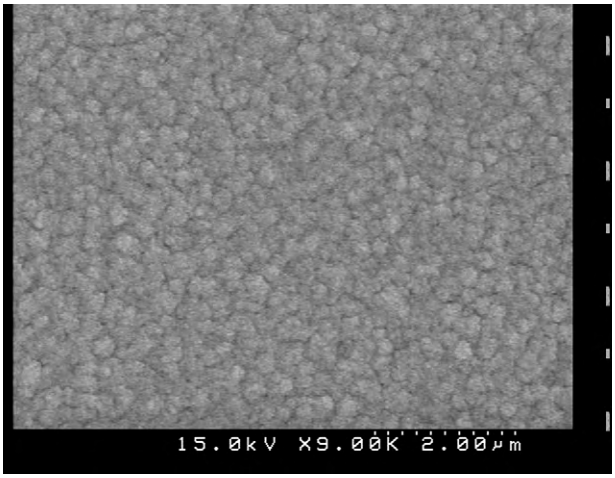

Fig. 3. Scanning micrograph of $CdSe_{0.62}Te_{0.38}$ film.

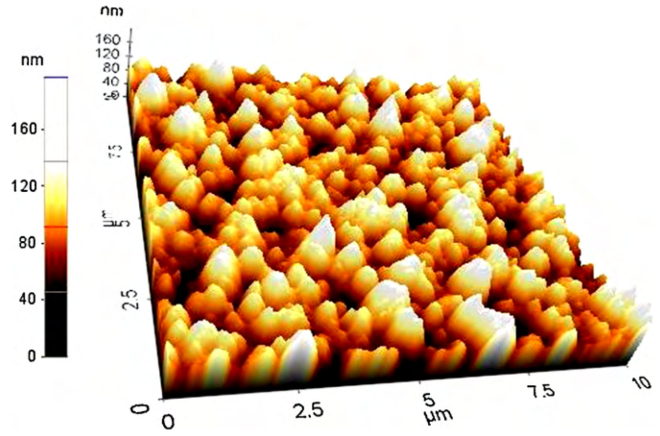

Fig. 4. AFM image of the electrodeposited CdSeTe thin film.

3.3. Optical study

Optical transmittance measurements of the films prepared with different selenium contents were obtained and these data were used to estimate the band gap energy. $CdSe_xTe_{1-x}$ is a direct band gap semiconductor like other II–VI semiconductors; therefore we used the following equation to find the band gap energy E_g.

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where A is a constant, $h\nu$ is the incident photon energy and α is the absorption coefficient of the film. The optical absorption data were used to plot a graph of $(\alpha h\nu)^2$ vs. $h\nu$, this plot is shown in Fig. 5. Extrapolation of the plots to x-axis gives the energy band gap of the deposited films of various compositions. The linearity of the $(\alpha h\nu)^2$ against $h\nu$ plot indicated the direct band gap nature of the films. The band gap of $CdSe_xTe_{1-x}$ is shifted to higher values when the Se concentration in the film increases and therefore band gap tailoring is achieved in the alloy films. The optical absorption spectrum shows band gap shift from 1.48 to 1.69 as the composition of $CdSe_xTe_{1-x}$ film varied from 0.2 to 0.8.

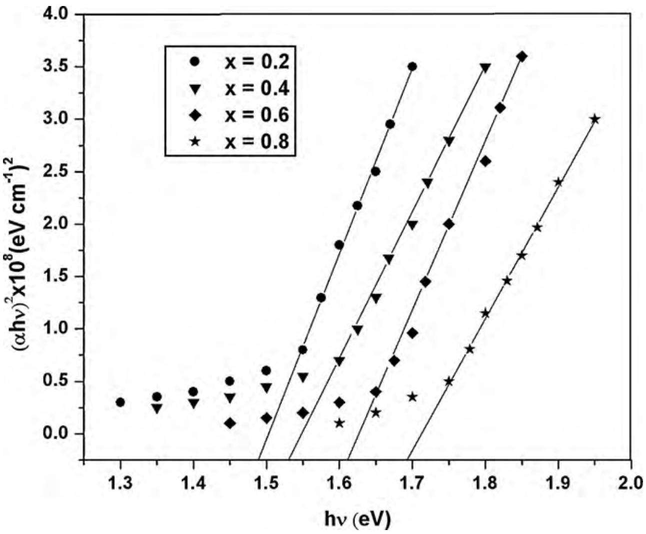

Fig. 5. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of $CdSe_xTe_{1-x}$ film with $x = 0.2$, 0.4, 0.6 and 0.8.

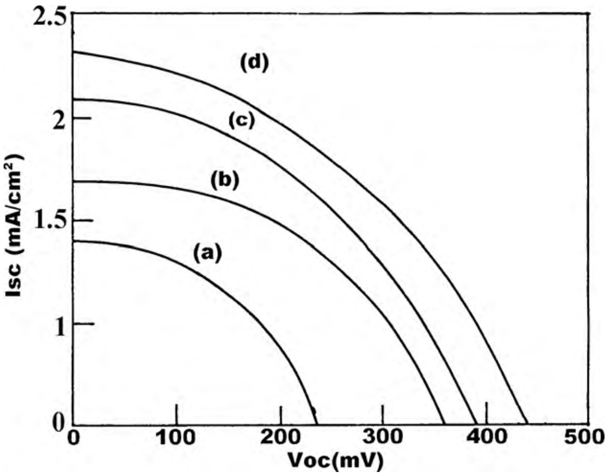

Fig. 6. Power output curves of $CdSe_xTe_{1-x}$ film for various Se concentrations (a) 0.2, (b) 0.4, (c) 0.6, and (d). 0.8.

Table 2
Photoelectrochemical cell parameters evaluated using the power output plot.

Film composition	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF	Efficiency (η%)
$CdSe_{0.2}Te_{0.8}$	235	1.4	0.5	1.65
$CdSe_{0.4}Te_{0.6}$	360	1.66	0.54	3.14
$CdSe_{0.6}Te_{0.4}$	392	2.1	0.48	3.95
$CdSe_{0.8}Te_{0.2}$	440	2.36	0.46.7	4.85

3.4. Photoelectrochemical study

Photoelectrochemical (PEC) solar cell was constructed comprising the as-prepared $CdSe_xTe_{1-x}$ films of various selenium compositions. The PEC solar cell power characteristics of $CdSe_xTe_{1-x}$ films of different Se composition are shown in Fig. 6.

The efficiency of solar cells is represented by the expression:

$$\eta = \frac{V_{oc}J_{sc}FF\,100}{P}$$

in which the fill factor (FF) is given by

$$FF = \frac{V_mJ_m}{V_{oc}J_{sc}}$$

where V_{oc} and J_{sc} are the open circuit voltage and short circuit current density, respectively. V_m and J_m are the voltage and current at the maximum power point of the solar cell and P is the input power. The photoelectrochemical (PEC) characteristics were obtained for all compositions of $CdSe_xTe_{1-x}$. The solar cell parameters obtained has been given in Table 2. The photoelectrode with composition of $CdSe_{0.8}Te_{0.2}$ exhibited highest output parameters; it was observed that the overall output has been increased as the selenium content increases in the material. It has also been found that the inclusion of Se in the film has improved V_{oc} and J_{sc} and hence solar conversion efficiency of the film has been improved with the inclusion of Se. The higher values of open circuit voltage at increased Se content may be attributed to the larger value of flat band potential. The inclusion of Se decreases the resistivity of the film; hence the short circuit current is higher than the CdTe [12]. Fig. 7 presents the trend of variation of efficiency with Se content. The increase is high for the variation of x from 0.2 to 0.4, the rate of increase is reduced as the content of Se increase, after the x value 6 the increase is less comparing to other values. Further studies, such as optimization and surface modification of electrodes to improve the efficiency of photoelectrochemical solar cells based on $CdSe_xTe_{1-x}$ thin films at various compositions are currently in progress.

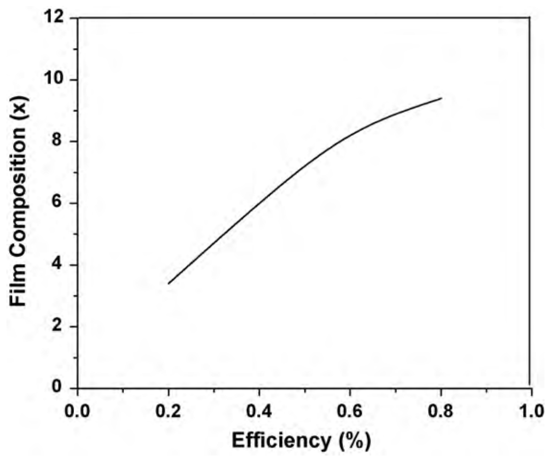

Fig. 7. Variation of PEC efficiency with film composition.

4. Conclusion

Thin films of $CdSe_xTe_{1-x}$ ($0 < x < 1$) have successfully been prepared by electrodeposition on SnO_2 coated glass substrates from an aqueous acid solution containing selenium and tellurium oxides in various amounts. The XRD and optical studies have proved the growth of CdSeTe thin film. All the films were adherent to the substrate and showed a hexagonal wurtzite structure. The increase of selenium content in $CdSe_xTe_{1-x}$ films has increased band gap of the alloy $CdSe_xTe_{1-x}$ films. The AFM and SEM studies of the grown films have shown good morphology of the film with grain size varying between 150 and 200 nm. The increase of Se content in the film has shown improved V_{oc} and J_{sc} and hence improved solar cell efficiency.

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