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Structural, optical and (photo)electrochemical properties of electrodeposited Cd-Zn-Se thin films

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Cadmium zinc selenide (Cd-Zn-Se) thin films have been prepared onto stainless steel and fluorine doped tin oxide (FTO) coated glass substrates by the electrodeposition technique. The structural, optical and photoelectrochemical properties of the films have been studied. The X-ray diffraction studies reveal that the Cd_{1-x}Zn_xSe (0 ≤ x ≤ 1) films are polycrystalline. It has also been found that the films deposited with x = 0.2 and 0.7 show relatively higher extent of single crystallinity than those deposited with other compositions. The estimated direct optical gaps are found to be in the range of 1.9 to 2.5 eV and it's value increases with an increase in the value of x. Photoelectrochemical characterization carried out using ferriferrocyanide electrolyte shows better performance for the films deposited with x = 0.2 and 0.7 compositions.

1 Introduction

In recent years, binary and ternary semiconductors have been attracting much interest in photovoltaics. Due to their good opto-electronic properties, Cd_{1-x}Zn_xSe materials are suitable for application in radiation detectors and laser screen materials in projection colour TV. Recently Natarajan et al. have prepared Zn_{1-x}Cd_xSe thin films and reported the influence of deposition parameters on the extent of single crystallinity of the material. The electrodeposition of CdSe and ZnSe has been studied widely.

Electrodeposition is a simple and an attractive method for the preparation of elementary, binary, ternary, quaternary and alloyed films. This method offers more advantages over the other methods as it is less expensive and simple in operation. It is an isothermal process, mainly depends on electrical parameters with the help of which film morphology, composition, etc. can easily be controlled.

In the present paper Cd_{1-x}Zn_xSe thin films have been prepared for various compositions (x) by electrodeposition method. The polarization curves are plotted to determine the deposition potentials. The films are characterized by X-ray diffraction (XRD), optical absorption and photoelectrochemical characterization techniques and the consequent results have been discussed.

2 Experimental Details

Cd_{1-x}Zn_xSe thin films were electrodeposited onto stainless steel and fluorine doped tin oxide (FTO) coated glass substrates (area, 1 cm²). The metallic substrates were mirror polished by zero polish paper and cleaned with detergent powder, brasso and finally by an ultrasonic cleaner, while conducting glass substrates were cleaned by 1M chromic acid and then by double distilled water. The economical and inert polished graphite plate (4 x 2 x 0.2 cm) was used as a counter electrode. The molarity of solutions of CdSO₄, ZnSO₄ and SeO₂ was kept constant at 0.025, 0.01 and 0.01M respectively. The pH of the bath was 5. The depositions were carried out from an unstirred solution at room temperature with potentiostatic conditions using a Saturated Calomel Electrode (SCE) as a reference electrode. The polarization curves were recorded for 0.025 M CdSO₄, 0.01M ZnSO₄ and 0.01M SeO₂ separately and then for the bath compositions of CdSO₄ and ZnSO₄ in the proportion 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0.

After deposition the films were washed with double distilled water and preserved in a desiccator. The film thickness was measured by the weight difference method. X-ray diffraction patterns of the films were obtained with the help of a Siemens diffractometer (PW-1710) using Cu-Kα radiation. Optical absorption studies of the films deposited potentiostatically on FTO-coated glass substrates in the wavelength range 350-850 were carried out using a UV-VIS-NIR spectrophotometer (Hitachi, Model-330). Photoelectrochemical charac-
terization were carried out using the cell configuration as \( \text{Cd}_x \text{Zn}_y \text{Se} | \text{1M KOH, 1M ferriferrocyanide | C} \).

3 Results and Discussion

The polarization curves were plotted to determine the deposition potentials of cadmium, zinc, selenium and cadmium zinc selenide (\( \text{Cd}_x \text{Zn}_y \text{Se} \) for \( 0 \leq x \leq 1 \)) from their respective baths on stainless steel substrates. The deposition potentials of Cd, Zn and Se, deposited on stainless steel substrates, are estimated from polarization curves (Fig. 1) and are shown in Table 1. The deposition potentials of \( \text{Cd}_x \text{Zn}_y \text{Se} \) for having bath compositions of \( \text{CdSO}_4 \) and \( \text{ZnSO}_4 \) in the volumetric proportion as 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0 were recorded from the polarization curves and are shown in Table 2.

The variation of film thickness with composition (x), for a constant current density of 0.5 mA/cm\(^2\), and deposition area of (1 cm\(^2\)) on FTO coated glass substrates was studied and is shown in Fig. 2. It is seen that the film thickness increases with increase in zinc composition (x). This may be attributed to the strong ionic bonding between zinc and selenium as compared to weak ionic bonding between cadmium and selenium. Strong ionic bonding between Zn and Se increases the film thickness as number of Zn ions (x) increases.

Fig. 3 shows the XRD patterns of \( \text{Cd}_x \text{Zn}_y \text{Se} \) thin films deposited of various compositions (x). The deposited films are polycrystalline in nature with mixed hexagonal (H) and cubic (C) phases of ZnSe and CdSe.

<table>
<thead>
<tr>
<th>Deposited film</th>
<th>Bath composition</th>
<th>Potential V/SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.025 M ( \text{CdSO}_4 )</td>
<td>-0.47</td>
</tr>
<tr>
<td>Se</td>
<td>0.01 M ( \text{SeO}_2 )</td>
<td>-0.67</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01 M ( \text{ZnSO}_4 )</td>
<td>-0.72</td>
</tr>
</tbody>
</table>

![Volatge, V/SCE](image)

Fig. 1 — Polarization curves for cadmium (\( \Delta \)), zinc (\( * \)), and selenium (\( \circ \)), on stainless steel substrates.
respectively for all the compositions. The observed \(d\) values are compared with the standard \(d\) values for C-CdSe (Ref. 10) and H-ZnSe (Ref. 11) in Table 3. A small change in \(d\) spacing of the C-CdSe and the H-ZnSe of about 0.02 A is observed accounting for the formation of ternary Cd-Zn-Se compound. The XRD patterns show the dominant orientations along the C-CdSe [(111) and (220)] and H-ZnSe [(102) and (202)] planes. The

Table 2 — Deposition potentials, \(V_{de}\), \(I_{sc}\) fill factor \((f/f)\) and efficiency \((\eta)\) for the films having different bath compositions of 0.025 M CdSO\(_4\), 0.01 M ZnSO\(_4\) and 0.01 M SeO\(_2\).

<table>
<thead>
<tr>
<th>Composition ((x)) Cd(_{1-x})Zn(_x)Se (pH=5)</th>
<th>Deposition potential (V_{de}) (V)</th>
<th>(I_{sc}) (mA)</th>
<th>(f/f) (%)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0, CdSe</td>
<td>-0.38</td>
<td>0.008</td>
<td>0.15</td>
<td>41.66</td>
</tr>
<tr>
<td>0.1</td>
<td>-0.48</td>
<td>0.305</td>
<td>1.46</td>
<td>44.46</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.45</td>
<td>0.324</td>
<td>1.97</td>
<td>55.22</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.38</td>
<td>0.138</td>
<td>1.32</td>
<td>51.38</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.37</td>
<td>0.046</td>
<td>0.24</td>
<td>49.27</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.40</td>
<td>0.095</td>
<td>0.59</td>
<td>49.50</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.43</td>
<td>0.174</td>
<td>1.08</td>
<td>50.28</td>
</tr>
<tr>
<td>0.7</td>
<td>-0.46</td>
<td>0.247</td>
<td>1.45</td>
<td>51.01</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.45</td>
<td>0.092</td>
<td>0.21</td>
<td>38.81</td>
</tr>
<tr>
<td>0.9</td>
<td>-0.46</td>
<td>0.042</td>
<td>0.01</td>
<td>33.33</td>
</tr>
<tr>
<td>1.0, ZnSe</td>
<td>-0.61</td>
<td>0.004</td>
<td>0.01</td>
<td>20.00</td>
</tr>
</tbody>
</table>

Fig. 2 — Variation of film thickness \((m)\) with composition \((x)\), at constant current density of 0.5 mA/cm\(^2\), for Cd\(_{1-x}\)Zn\(_x\)Se films.
Fig. 3 — XRD patterns of Cd$_{1-x}$Zn$_x$Se thin films on stainless steel substrates
The bandgaps were determined by extrapolating the straight portion to the energy axis. It has been found that the direct bandgap energy varies from 1.9 to 2.5 eV with an increase in the value of \(x\) from 0 to 1 (Fig. 5). Since the bandgap energies of CdSe and ZnSe are 1.73 and 2.58 eV respectively\(^{13}\), the energy bandgaps of Cd\(_{1-x}\)Zn\(_x\)Se, owing to similarity to band structure of the two compounds, must increase with increasing value of \(x\) between two limits\(^1\).

Photoelectrochemical characterization of Cd\(_{1-x}\)Zn\(_x\)Se thin films, deposited onto the stainless steel substrates, has been carried out using 1M KOH + 1M ferric ferrocyanide as an electrolyte. Cd\(_{1-x}\)Zn\(_x\)Se as a photo-anode, carbon as a counter electrode and a tungsten filament lamp (80 mW/cm\(^2\)). The short circuit current (\(I_{sc}\)) and open circuit voltage (\(V_{oc}\)) for the film of each composition are recorded. It has been found that, for \(x = 0.2\) and 0.7, the Cd\(_{1-x}\)Zn\(_x\)Se film shows relatively higher values of \(I_{sc}\) and \(V_{oc}\) in ferricyanide (pH=14). The variation of \(I_{sc}\) and \(V_{oc}\) with composition is shown in Fig. 6. Table 2 shows the values of \(I_{sc}\) and \(V_{oc}\) for each composition.

It has also been found that, the values of \(I_{sc}\) (1.97 mA) and \(V_{oc}\) (0.32 V) for \(x = 0.2\) are higher than the values of \(I_{sc}\) (0.53 mA) and \(V_{oc}\) (0.17 V) for \(x = 0.7\), which may be attributed to the preferred orientation, greater size of the micrograins and formation of better stoichiometric compound at \(x = 0.2\) than at \(x = 0.7\. Relatively higher XRD peak intensities at \(x = 0.2\) than at \(x = 0.7\) support these results.

The calculations lead to the fill factor (\(ff\)) of 55.22\% and power conversion efficiency (\(\eta\)) of 0.44\% for the film deposited at \(x = 0.2\). Table 2 reports the values of \(ff\) and \(\eta\) for the films deposited at each composition. The very low efficiency in this investigation might be due to the absorption of light by the electrolyte, high series number of planes observed at \(x = 0.2\) and 0.7 are relatively more in comparison with planes observed for other compositions. The (111) plane of C-CdSe starts appearing, with relatively maximum intensity at \(x = 0.2\) and it's intensity continuously goes on decreasing as composition (\(x\)) increases. At \(x = 0.9\), the (111) plane completely disappears. The (220) plane of C-CdSe starts appearing right from beginning; with continuously increase in intensity; becomes maximum at \(x = 0.7\) and decreases thereafter. The intensity of the (102) plane of H-ZnSe increases with composition and is found to be maximum for \(x = 0.2\) which decreases with further increases in composition. The intensity of (202) plane of H-ZnSe is found to be maximum at \(x = 0.2\) and \(x = 0.7\) only. The peaks in the diffractogram at \(x\) other than 0.2 and 0.7 are relatively weak and this reflects the insufficient growth of the samples at these compositions. The huge background visible in X-ray spectra for \(x = 0.1\), 0.2, 0.3 and 0.6 may have appeared due to amorphous phase of Se in addition to C-CdSe and H-ZnSe. On the other hand, the intense peaks at \(x = 0.2\) and 0.7 reveal clear evidence of formation of better stoichiometry of the compound as a result of the enhancement of grain growth at these compositions. The most striking aspect of the present result is that highly oriented growth becomes possible only at \(x = 0.2\) in the (102): H-ZnSe direction.

Optical absorption of Cd\(_{1-x}\)Zn\(_x\)Se films deposited onto FTO-coated glass substrates has been studied in the wavelength range of 350-850 nm at room temperature. The value of absorption coefficient is of the order of 10\(^4\) cm\(^{-1}\) for all compositions. In order to estimate the bandgap energy (\(E_g\)) of Cd\(_{1-x}\)Zn\(_x\)Se films, the plots of \((h\nu)^2\) versus \(h\nu\) are plotted in Fig. 4 shows the plot of \((\alpha h\nu)^2\) against \(h\nu\) for the typical Cd\(_0.3\)Zn\(_{0.7}\)Se thin film.
Fig. 4 — Plot of $(h\nu)^2$ against $h\nu$ for Cd$_{0.8}$Zn$_{0.2}$Se thin film

Fig. 5 — Optical gap (direct) $E_g$ versus composition ($x$) for Cd$_{1-x}$Zn$_x$Se thin films
resistance of the PEC cell, low thickness of the film and interface states, which are responsible for the interactive recombination\textsuperscript{12,13}. One of the major problems in utilizing PEC cells is the absence of space charge region at the electrode-electrolyte interface. Under these circumstances, photo-generated charge carriers can move in both directions. It is reported that\textsuperscript{14}, the photo-generated electrons in \textit{n}-type CdSe thin film electrode either recombine readily with holes or leak out into the electrolyte, instead of flowing through the external circuit.

4 Conclusions
Cadmiun zinc selenide thin film preparation onto stainless steel and FTO coated glass substrates is feasible. The prepared films are polycrystalline in nature with cubic and hexagonal phases. The estimated values of direct bandgap energies are found to be increased with an increase in zinc composition. The PEC cell formed using ferriferrocyanide electrolyte shows better performance with \( \text{Cd}_{0.8}\text{Zn}_{0.2}\text{Se} \) photo-electrode.

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References