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Zinc doped polycrystalline CdSe films for solar energy conversion

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Abstract

The physical properties of semiconductors define to a great extent the performance of photoelectrochemical (PEC) cells. With a band gap of 1.7 eV, cadmium selenide is an attractive candidate as photoelectrode in PEC cells for the conversion of light into electricity. Polycrystalline films are used for low-cost cells. CdSe films are prepared on a titanium substrate by the electrocodeposition technique from a solution of SeO_2, $CdSO_4$ and H_2SO_4 in galvanostatic conditions, then annealed at 400 °C. Chemical modification of semiconductor surfaces by metal ions has been found to improve the performance of photoelectrodes. Zn ion incorporation on the CdSe film surface was achieved by dipping the film in aqueous solution of $ZnSO_4$ followed by heating in air. The preparation conditions were optimized to give the best performance. The photovaltaic activity of the films was studied with a polysulphide electrolyte using graphite as a counter electrode and a 200 Watt tungsten lamp as the light source.

Addition of Zn ions at the surface produces favourable states in band gap, enhancing charge transfer kinetics at the interface. On heating, Zn diffuses through grain boundaries, reducing recombination centres for majority carriers, thus increasing diffusion length and so photocurrent. In the CdSe lattice, Zn replaces Cd ions which causes an increase in band gap since ZnSe has a band gap higher than CdSe. Hence a small amount of Zn reduces I_{sc} due to an increase in band gap, but as the Zn concentration is increased, greater band bending is obtained, increasing V_{oc} and improving overall performance.

Keywords: Semiconductors; Photoelectrochemical cells; cadmium selenide

1. Introduction

The photoelectrochemical (PEC) properties of semiconductor electrodes have been the subject of many studies, strongly encouraged by the prospect of using the photoelectrochemical systems for solar energy conversion. The major advantage of PEC cells is the ease of junction formation. By using a surface manipulation technique on the semiconductor electrode, the conversion efficiency can also be enhanced [1]. Although the majority of scientific investigations have been performed on single crystalline materials, it is recognized that any large scale application must rely on less expensive polycrystalline materials prepared in thin film form which can be scaled up into an industrial process.

Mixed metal chalcogenides are currently attracting attention because of their importance from the point of view of a variety of optoelectronic and photovoltaic applications [2]. The physical properties of Semiconductors define to a great extent the performance of photoelectrochemical cells. In recent years cadmium selenide photoelectrodes have been the object of considerable interest due to their high stability and efficiency. With a band gap of 1.7 eV it is a widely studied material for a photoelectrode in a PEC cell for conversion of light into electricity using terrestrial solar radiations [3]. Cadium selenide single crystals have been shown to exhibit a conversion efficiency as high as 10–15% [4] in polysulphide solution; whereas polycrystalline CdSe exhibit lower efficiency. In spite of that polycrystalline CdSe is still considered to be attractive for the conversion of light into electricity becuse thin films of CdSe can be prepared by several convenient methods [5]. Electrodeposition is a simple and cost-effective technique for the preparation of polycrystalline thin films.

Chemical modification of semiconductor surfaces by metal ions is known to enhance open circuit voltage at the electrolyte interface and also stabilises the surface against dissolution [6]. Two different explanations are suggested: (i) metal ions interact with surface states and remove Fermi level planning, and (ii) metal ions shift the surface Fermi level in the direction to enhance the barrier height [7]. The PEC solar cell parameters of electrocodeposited n-CdSe films on titanium substrates and the effect of zinc ion incorporation on the CdSe surface have been reported here.

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2. Experimental details

The cadmium selenide films were prepared by electrocodeposition onto 99.99% pure titanium substrate. Approximately 1 mm thick titanium foil was cleaned and washed successively with acetone and distilled water and used as cathode in a solution of SeO_2, 0.1 M $CdSO_4$ and 0.5 M H_2SO_4. Deposition was carried out at room temperature under galvanostatic condition; and the SeO_2 concentration, current density and deposition time were optimized for best photoresponse. The film thickness was measured gravometrically. After electrocodeposition, the films were annealed at 400 °C for 2.5 h.

Zinc ion incorporation at the CdSe film surface was achieved by dipping the films in an aqueous solution of $ZnSO_4$. This was followed by gentle washing in distilled water and heating in air at 100 °C for half an hour, as reported previously [8]. The concentration and temperature of $ZnSO_4$ solution and the duration of dipping time were also optimized for best performance.

The photoelectrode was prepared by applying common epoxy on the back and sides of the titanium substrate, leaving 1×1 cm^2 of semiconductor surface. Spot welded copper leads at the back of the titanium substrate were used for electric connection. Photovoltaic activity of the films was studied in polysulphide electrolyte consisting of NaOH, Na_2S and S (1 M each) in standard two electrode configuration in a pyrex glass vessel. A graphite plate (1×4 cm^2) was used as counter electrode. Digital multimeters (Philip model) were used to record current voltage behaviour without light and under illumination by a 200 W tungsten lamp. The photocurrent and photovoltage were determined by considering the initial values as zero i.e. taking I (dark) = 0 and V (dark) = 0 which were of the order of 1 μA and 1 mV respectively. The cell parameters were determined at various light intensities.

3. Results

The parameters of PEC solar cells are found to increase by 1–2 orders of magnitude by optimizing the preparation conditions of electro-codeposited CdSe films. The experiments carried out in our laboratory give the following optimum conditions for photoresponse of CdSe films in polysulphide electrolyte PEC cells:

1. Concentration of SeO_2	as 0.03 M
2. Current density	as 7 mA cm^{-2}
3. Deposition time	as 45 minutes which gives film thickness 4 μm.

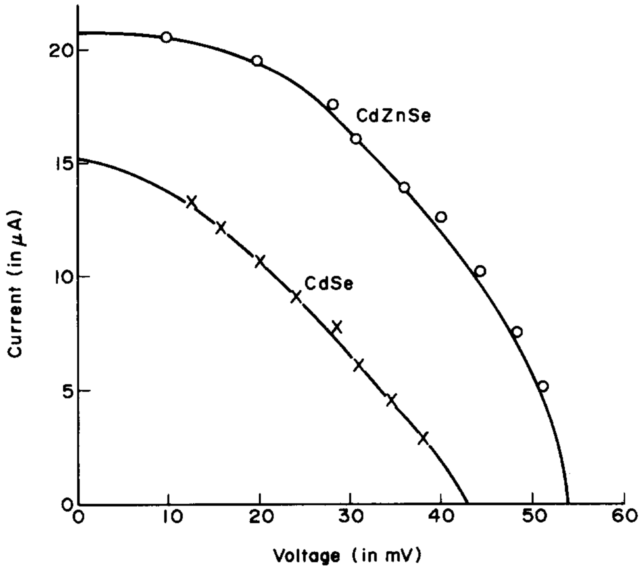

Fig. 1. I–V characteristics,

These results are in agreement with those reported by Bandyopadhyay and Chaudhari [9]. A typical I–V characteristic is shown in Fig. 1 and the cell parameters are given in the Table 1.

The incorporation of Zn ions into CdSe film is found to improve the performance of the cells considerably. The optimum preparation conditions are found to be as follows:

1. Concentration of $ZnSO_4$ solution	1.5 M
2. Temperature of $ZnSO_4$ solution	70 °C
3. Dipping time duration	60 min.

The I–V characteristics and solar cell parameters for a typical CdZnSe photoanode-based solar cell is shown in Fig. 1 and Table 1 respectively. The quality factor (n) has been determined from the plots between V_{oc} and $\ln(I_{sc})$ values at different light intensities.

4. Discussion

An important advantage of photoelectrochemical solar cells, compared with the solid state devices is that the junction is produced simply by immersing the semiconductor in the solution. Moreover the light is ab-

Table 1
Solar cell parameters

Parameter	CdSe	$Cd_{1-x}Zn_xSe$
Open circuit voltage (V_{0c}) (mV)	42.5	53.5
Short circuit current (I_Sc) (μA)	16.2	20.8
Maximum power output (P_{max})(nW)	214	497
Fill factor (f.f.)	0.33	0.45
Quality factor (n)	2.9	4.5

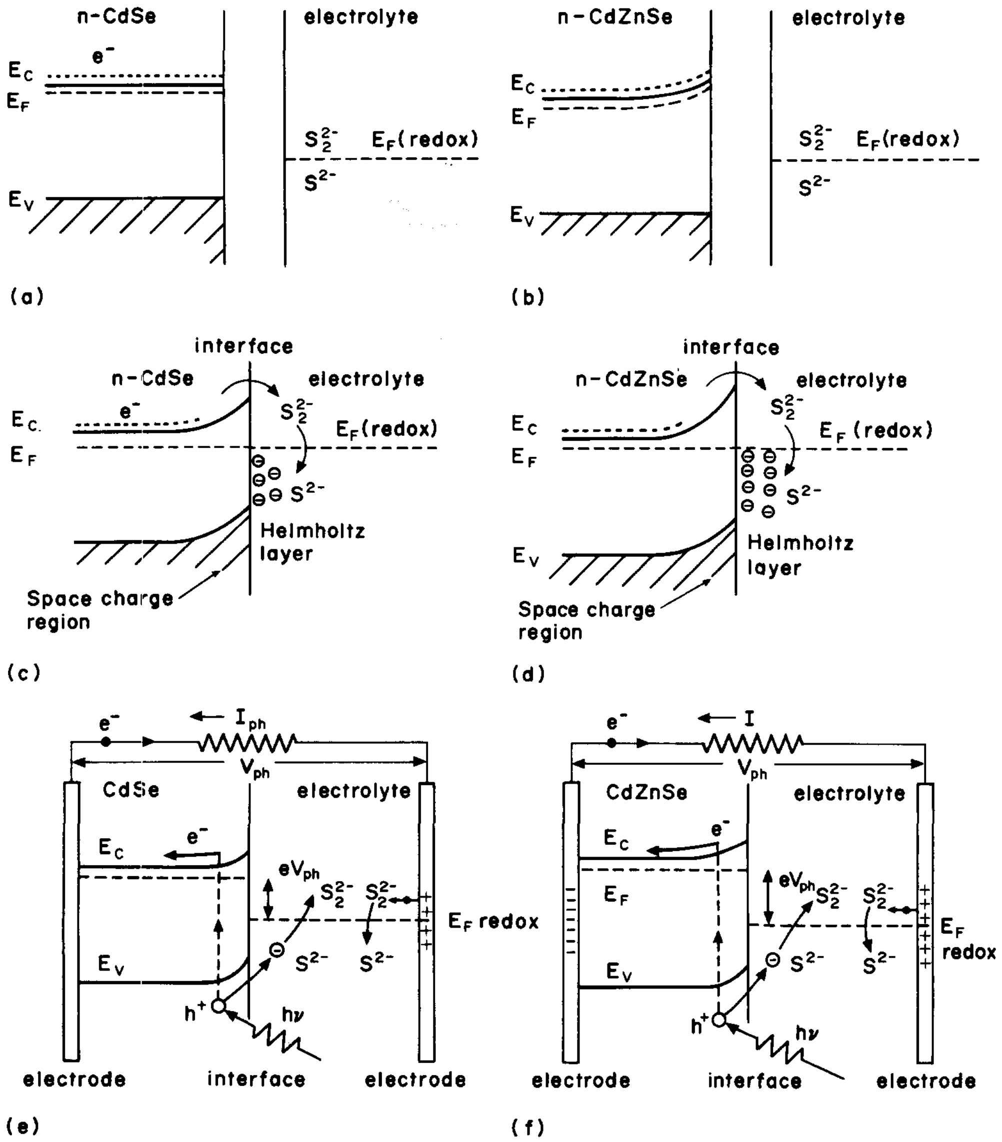

Fig. 2.

sorbed right at the interface, so that photogenerated carriers have to move only a short distance before they react. When a semiconductor is immersed in a solution, electronic and ionic exchange processes occur at the interface because of the difference in the electron affinity or electrochemical potential and then a thermodynamic equilibrium is established. The preparation condition of films play a vital role in controlling their photoelectric properties.

Studies reported by Sanjeeviraja et al. [10] on CdSe films obtained by a similar method as used in the present investigation, show that the films are *n*-type owing to Se vacancies (Cd donors). XRD data indicated a polycrystalline nature with grain size 20–40 nm. Electron micrographs have shown that the films retain their microcrystalline structure down to a layer thickness of 20 nm with a crystallite size of about 20 nm [11]. Amorphization occurs when the layers are thin.

The minimum energy gap of 1.74 eV of bulk CdSe suggests the onset of optical absorption at 714 nm. Nair and Nair [12] have found that the onset of optical absorption in similar films occurs near 620 nm showing increase in band gap up to 0.5 eV higher than a single crystal sample. This has been explained on the basis of quantum size effect which arises due to the small crystalline size of the order of nanometers. Similar increase in optical band gap has also been observed in CdS films.

Dipping of the CdSe films in aqueous solution of $ZnSO_4$ causes deposition of zinc on the frontal layers. Penetration of Zn within the bulk takes place on heating. The electrodeposited CdSe films, being polycrystalline in nature, have internal surfaces in the form of grain boundaries. These represent regions of weak chemical bonds and introduce localised states which may capture majority carriers. It is well known that the grain boundary diffusion coefficient is usually 10^3-10^4 times greater than the bulk diffusion coefficient. Hence chemiabsorption of zinc within the CdSe bulk is mediated predominantly via grain boundaries. This may reduce grain boundary recombination and thus increase the diffusion length improving the performance of the cell. By doping Zn in CdSe, Zn ions replace Cd ions in the lattice and it may be considered as a solid solution of CdSe and Zn [13]. Hence the films may be visualised as a solid solution having maximum concentration of ZnSe at the surface and decreasing in deeper layers. The forbidden band gaps of CdSe and ZnSe are 1.7 eV and 2.7 eV respectively. In the solid solution, the band gap is increased due to the presence of ZnSe depending on its concentration and therefore band bending occurs at the surface. Mandal [7] has shown by measurement of contact potential difference (CPD) that zinc doping at the surface of CdSe films shifts the surface Fermi level in a direction to enhance the barrier height which is in agreement with the increase in open circuit voltage of solar cells. This can be attributed to additional surface charge provided by zinc ions. Fig. 2(b) shows the energy level diagram on Zn doped CdSe films indicating the band bending in case of $Cd_{1-x}Zn_xSe$ films.

When the film comes into contact with polysulphide (S^{2-}/S_2^{2-}) solution, charge transfer occurs at the interface. The electrons from n-type semiconductor film reduce the oxidised species of solution i.e.

$$S_2^{2-} + e^- \rightarrow 2S^{2-}$$

The loss of electrons from semiconductor to electrolyte creates a positive space charge region up to a depth of 5–200 nm [14]. This causes band bending in the semiconductors as shown in Fig. 2(c) and (d). The positive charge on the semiconductor is compensated by negative ions present in the electrolyte on the other side of the interface forming a Helmholtz layer of a thickness of several anstroms (~1000 Å). Greater bending of bands will occur in CdZnSe films as compared to CdSe because of shifting of surface Fermi level.

When the film is illuminated, the electron-hole pairs produced near the surface in the depletion region are separated due to the space charge field. The electrons move towards bulk and the holes, reaching the interface, react with the reduced species:

$$2S^{2-} + h^+ \rightarrow S_2^{2-}$$

Due to illumination the bands unbend (Fig. 2(f)) and the Fermi level of semiconductor (E_F) shifts [15]. This leads to a change in electrode potential. The change i.e. the photopotential, is equal to the shift in the Fermi level for illuminated electrodes with respect to nonilluminated case divided by the charge of electron. Higher photopotential is obtained in the case of GdZnSe because of greater band bending.

Thus zinc doping on the surface of electrodeposited n-CdSe films improves the performance in polysulphide electrolyte photoelectrochemical solar cells.

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