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Structural and Photo-electrochemical (PEC) Cell Properties of $Cd_{1-x}Zn_xSe$ Films

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ABSTRACT

In the present work, cadmium zinc selenide ($Cd_{1-x}Zn_xSe$) ternary alloy compounds were prepared on glass substrates for various concentrations by Electron beam evaporation method (PVD: EBE), under a pressure of 1 x 10^{-5} mbar. Structural, spectral response and photo-electrochemical properties of $Cd_{1-x}Zn_xSe$ films have been studied. Structural studies by X-ray diffractogram (XRD) revealed the polycrystalline nature of the as-prepared films. Full Width Half Maximum (FWHM) value was observed from the XRD pattern; the same was used to find the microstructure properties of the films. XRD characterization of the films indicated hexagonal structure with strong preferential orientation of the crystallites along (0 0 2) direction. The normalized spectral response curve has shown that the peaks were shifted to higher wavelength side with incorporation of higher zinc content into the CdSe lattice. The analysis of I-V curve for $Cd_{0.8}Zn_{0.2}Se$ films has given the highest values for V_{OC}, I_{SC}, FF and η%. Conversion efficiency was continuously decreasing from 4.5 to 1.93 with increasing zinc content from 0.2 to 0.8.

Keywords: Electron beam evaporation; PEC properties; Solar cells.

1. INTRODUCTION

The wide band gap II–VI CdSe and ZnSe type semiconductor thin films have significant attraction during the last decades due to their wide applications in variety of opto-electronic devices such as lasers (Esparza-Ponce *et al.* 2009), sensors (Ramaiah *et al.* 2001), transistors (Wang *et al.* 2006), photoelectrodes (Winder *et al.* 1995), light emitting diodes (Hankare *et al.* 2004; Mariappan *et al.* 2012), photocatalysts (Wang *et al.* 2013), optical wave guides (Banfi *et al.* 1995), and solar cells (Van Calster *et al.* 1988; GRUSZECKI *et al.* 1993; Deshmukh *et al.* 1997; Gur *et al.* 2006; Kniprath *et al.* 2009). As compared to III-V materials, II-VI wide gap materials such as CdSe, ZnSe and ZnS have considerable amount of higher excitonic binding energies. Recently, there have been several studies on photo-conductivity, photo-conducting process, photo-diodes, photo-electrochemical solar cells (PEC), photovoltaic cells, etc. This type of solar cells comes under semiconductor-liquid junction based electrochemical solar cells. Harvesting solar energy has attracted the attention of scientists, economists and technologists of the world to counter the energy crisis. Lot of efforts have been employed towards developing new and better solar energy conversion devices. A high degree of sophistication has already been achieved in the fabrication of p-n junction solar cells. The main problem that posed challenge to solar energy research is solar energy storage. Ever since Fujishima and Honda (Fujishima *et al.* 1972) used a semiconductor electrode dipped in a liquid electrolyte to photo-electrolyte water and obtained hydrogen (a transportable form of energy), the solar energy research has gained a large momentum. In 1983, Gerischer (Gerischer *et al.* 1983) succeeded in direct conversion of solar energy into electricity, using the photo-electrochemical solar cells that offered both energy conversion and energy storage. The promise of photo-electrochemical solar cells as an efficient source for clean power has remained unrealized because of non-availability of low band gap non-corrosive photo effective materials.

Effort is now being made to prepare a material by alloying two different materials, one exhibiting low band gap and other with a high band gap such that high efficiency and photo-electrochemical stability may be achieved simultaneously. A photo-electrochemical effect is defined as one in which the irradiation of an electrode electrolyte system produces a change in electrode potential (open circuit) or a change in current flowing in the external circuit (short circuit). There are several advantages of using PEC solar cells over conventional solid-state cells: PEC devices can be easily fabricated unlike photovoltaic devices; the band bending can be varied conveniently by suitable choice of electrolyte and cell variable; the differential thermal variation associated with a solid-solid junction are not present; *in-situ* storage facility; and the possibility of fabricating hybrid systems using both photovoltaic and photothermal effects.

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Chandra and Pandey (Chandra *et al.* 1980) achieved sophistication in the fabrication of PEC. The added advantages of PEC are that there is no lattice mismatch and controlling of the barrier height. Hence, PEC has received considerable attention as an alternative to solid-state solar cells for solar energy conversion purpose. Licht *et al.* 1997 brought out the need for testing new materials as photoelectrodes for PEC. The efficiency and suitability of PEC cells are strongly dependent on the preparation of the photo-electrode and the electrolyte used. By systematic modification of the potassium cyanide electrolyte, Chandra Babu *et al.*1994 described the feasible efficiency enhancement process such as electrode surface modification and electrolyte modification which enhanced the efficiency of n-CdInSe$_2$/Polysulphide cell to 12%.

In the present article, principle and working of PEC cells were outlined. In addition, the behavior of PEC cells fabricated using EB evaporated ZnSe, CdSe and $Zn_{1-X}Cd_XSe$ thin films were studied thoroughly and various semiconductor parameters were evaluated and summarized. An attempt was made to improve the performance of these PEC devices using surface modifications of the electrodes.

2. EXPERIMENTAL PROCEDURE

Amongst the various deposition techniques available physical vapor deposition method of electron beam evaporation technique is the scarcely used method for the deposition of device quality II-VI thin films, because it affords flexibility in the control over various deposition parameters and easy adaptability of this technique for commercial purposes. As far as the electron beam evaporation is concerned, very thin films with a good surface smoothness can be obtained and there is no restriction on the type of the substrate. A well-cleaned microscopic and FTO-coated glass substrates have been used for the preparation of semiconductor thin films by electron beam evaporation technique. CdSe (Aldrich, 99.99%) and ZnSe (Aldrich, 99.99 %) binary compounds were mixed in various atomic proportions and used as the precursor powder pellet for depositing the film. Before making the pellets, the powder mixtures were ground in an agate mortar for 3 hours to get uniformly mixed powders. The CdZnSe pellets heated at 100 °C for one hour at a pressure of 10 tons/cm^2. The pellets were used as a target material to prepare the $\mathrm{Cd_{1-x}Zn_xSe}$ thin films on well-degreased microscopic glass plates. The surface of the $\mathrm{Cd_{1-x}Zn_xSe}$ pellets were bombarded by 180° deflected electron beam with an accelerating voltage of 6 kV and a power density of about 1.5 kW/ccm^2. This article presents the structural, spectral response and PEC solar cell characteristics. The structural properties of the films were studied by JEOL JDX X-ray diffractometer (XRD) using CuKα radiation ($\lambda = 1.5418\, A^{\circ}$) with Ni filter.

2.1 PEC Experimental set-up

The schematic representation of a PEC set-up used is shown in Fig. 1.

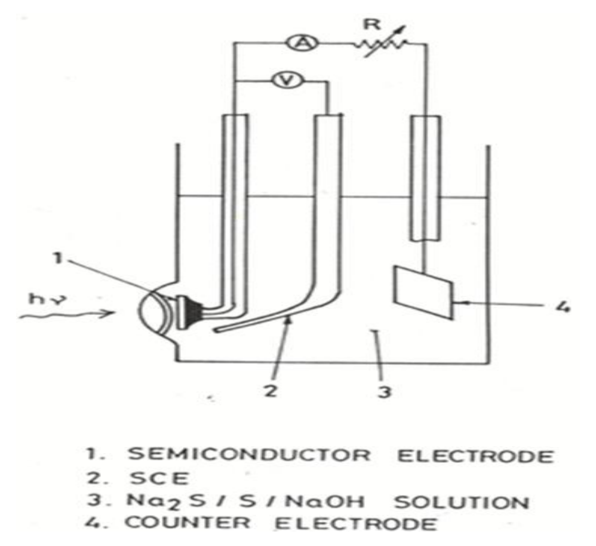

Fig. 1: Schematic representation of a Photo-Electrochemical Cell (PEC) set-up

The electrolyte is taken in a specially designed beaker and the electrodes ($\mathrm{Cd_{1-x}Zn_xSe}$ thin films electro synthesized onto titanium and counter electrode platinum) were dipped into it. A quartz window in the beaker could allow the light from the source to the semiconductor surface. The saturated calomel electrode was used as the reference electrode. The electrodes were kept at distance of 1 cm apart and the reference electrode, luggin capillary was kept adjacent to the semiconductor electrode. All the portions of the beaker were covered with black paint and the entire system was kept in a black box to reduce the reflection losses.

2.2 Electrolyte preparation

The electrolyte comprised 1 M sodium sulphide (Na_2S), 1 M sulphur (S), 1 M sodium hydroxide (NaOH) and water. The aqueous electrolyte preparation was done by adding sulphur, sodium sulphide and sodium hydroxide in succession. Great core has been taken to confirm the dissolution of sulphur before adding the other species. The electrolyte was stored in a light protected container before use.

2.3 Electrode preparation

Electrodes of $\mathrm{Cd_{1-x}Zn_xSe}$ thin films were used as photo anodes. The ohmic contacts, made with silver epoxy, was used to attach the metal lead made of copper. About 0.1 cm^2 area of the film surface was exposed to the electrolyte and the remaining portion of the semiconductor films were made insulating using araldite.

The samples were mounted onto a glass holder. A glass cell with quartz window was used for the purpose of PEC experiments.

To study the spectral and power characteristics of the $Cd_{1-x}Zn_xSe$ thin film electrodes synthesized by electron beam evaporation, Na_2S-S-NaOH has been taken as the redox electrolyte. The electrodes were dipped in the electrolyte until equilibrium is reached. The current and voltages were measured in dark and under-illumination with different light intensities. The intensity of the incident radiation was varied and the current and the voltages were recorded. A graph was drawn between current and voltage (I- V plot). A tangent was drawn to the curve and at this point the maximum photo voltage (V_{mp}) and photo current (I_{mp}) were measured.

3. RESULTS AND DISCUSSION

3.1 Structural Properties of $Cd_{1-x}Zn_xSe$ Semiconductor thin Films

XRD patterns of the EB-evaporated $Cd_{1-x}Zn_xSe$ thin films were recorded to study the nature, phase and structure with different zinc content (x) introduced into the CdSe matrix. Fig. 2 shows the XRD spectra of $Cd_{1-x}Zn_x$ Se films with x = 0.2, 0.4, 0.6 and 0.8. The sharp and well-defined peaks indicate the polycrystalline nature of all the films. One high intense peak was observed at $2\theta = 25.62^o$ corresponding to (002) reflection and another peak very close to it at $2\theta = 24.18^o$ which is assigned to (100) with reduced intensity.

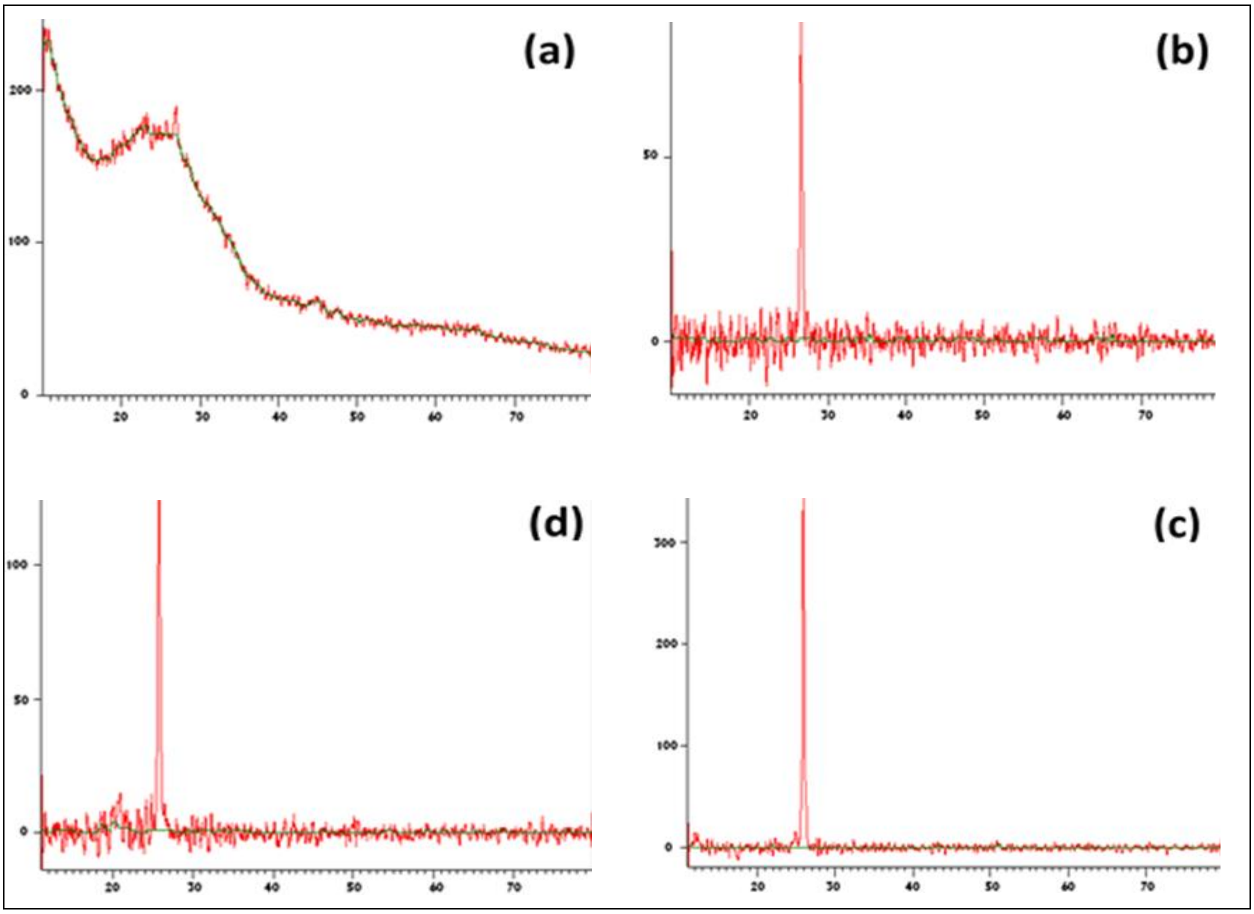

Fig. 2: XRD spectra for $Cd_{1-x}Zn_xSe$ films with: a) x = 0.2 b) x = 0.4 c) x = 0.6 and d) x = 0.8

3.2 PEC Solar Cell Properties Using $Cd_{1-x}Zn_xSe$ Solid Solutions

CdZnSe is an interesting alloy of the ternary II - VI semiconductors which can be used as an emission and absorption device in the UV – Vis. region. However, limited studies were found on $Cd_{1-x}Zn_xSe$ thin films prepared by electrochemical method. CdSe is usually obtained in hexagonal phase and ZnSe in cubic phase. CdSe is obtained as n-type. ZnSe is obtained both as 'n' and 'p' type during synthesis of polycrystalline thin films. It was observed that ZnSe was a more stable photoelectrode when compared to CdSe which was unstable but at the same time it exhibited higher efficiencies in PEC solar cells. Alloying of CdSe with ZnSe may result in photoelectrodes with improved efficiency and stability.

Photo-electrochemical solar cells of CdSe and ZnSe films, in particular CdSe films, have been largely investigated in terms of improving power efficiency, corrosion resistance and material utility. In this regard, protective and properties –modifying barrier films with nano crystallites, such as other II – VI materials, have been studied to stabilize and improve n-type CdSe (1.72 eV) electrodes in PEC solar cells. In this regard, the variable band gap systems prepared by vacuum-based techniques provide the necessary solution. For this purpose, ZnSe incorporation in CdSe films may provide a barrier to electrochemical corrosion and enhance the PEC solar cell conversion efficiency through its influence on open circuit voltage. In the present study, $Cd_{1-x}Zn_xSe$ films with nano-grains were deposited on conducting substrates (SnO_2 on glass) at 100 °C with a thickness of about 300 nm. Their spectral response and PEC solar cell characteristics were studied.

3.3 Spectral Response Studies of $Cd_{1-x}Zn_xSe$ Films

$Cd_{1-x}Zn_xSe$ films with nano-crystallites were prepared with zinc content, x = 0.2, 0.4, 0.6 and 0.8, and their spectral responses were observed. The spectral response study of the $Cd_{1-x}Zn_xSe$ thin films electrode / polysulphide / cell photo-electrochemical solar cell was carried out by measuring short-circuit current I_{sc} as a function of band gap. Before measuring the short circuit current, the cell was kept inside a dark room for a few hours and the response was measured using progression form longer wavelength to shorter wavelength. The normalized spectral response curve is shown in Fig. 3. The spectral responsivity has shown that the peaks were shifted to higher wavelength side with the incorporation of higher zinc content into the CdSe lattice. This result has confirmed the solid solution formation between CdSe and ZnSe binary compounds.

3.4 PEC Solar Cell Output Studies of $Cd_{1-x}Zn_xSe$ Films

The I-V output values were plotted and shown in Fig. 4 for $Cd_{1-x}Zn_xSe$ films with x = 0.2, 0.4, 0.6 and 0.8. The analysis of I-V curve for $Cd_{0.8}Zn_{0.2}Se$ films, has given the highest values for V_{OC}, I_{SC}, FF and η%. Conversion efficiency was found continuously decreasing from 4.5 to 1.93, with increase in zinc content, x, from 0.2 to 0.8. The variation of I_{SC}, V_{OC}, FF and η% were given in Fig. 5 (a, b, c, d) respectively. Increase of output power with zinc incorporation was reported for CdSe / ZnSe films deposited by electrodeposition technique (Bouroushian *et al.* 2006).

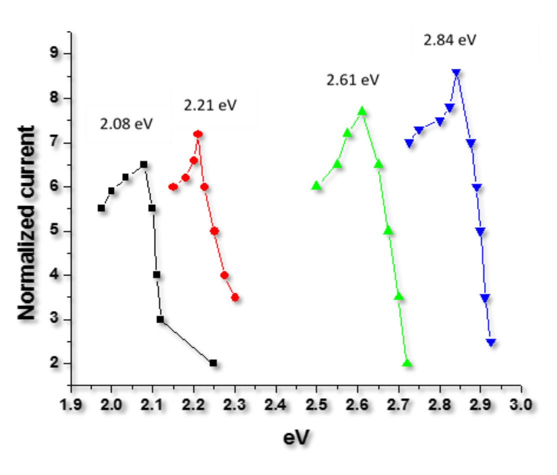

Fig. 3: Spectral response curves of EB-evaporated $Cd_{1-x}Zn_xSe$ films deposited at different substrate temperatures

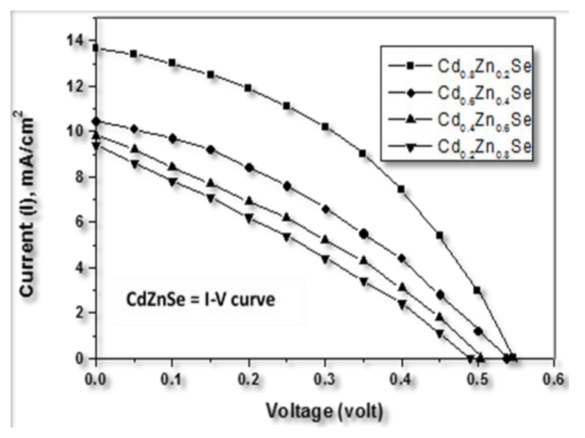

Fig. 4: I-V curve of $Cd_{1-x}Zn_xSe$ films with x = 0.2, 0.4, 0.6 and 0.8

Similar results were reported for zinc ion-treated CdSe materials by (Fitzmorris *et al.* 2012) the incorporation of zinc into the CdSe lattice, resulting in a shift of Fermi level in a direction to enhance the barrier height. Consequently, the output voltage was increased to more than 0.52 V and the film surface was stabilized against dissolution. However, when Zn content was increased beyond x = 0.2, a large reduction in PEC solar cell performance happened. This was mainly due to the increased resistance nature of the films and also due to the enhanced band gap values compared to either CdSe or $Cd_{0.8}Zn_{0.2}Se$ films. This will reduce the range of solar photon absorption considerably, thereby reducing the current output largely and hence FF and conversion efficiency as well.

Table 1. Lattice parameter values derived from XRD spectra for $Cd_{0.8}Zn_{0.2}Se$, $Cd_{0.6}Zn_{0.4}Se$, $Cd_{0.4}Zn_{0.6}Se$ and $Cd_{0.2}Zn_{0.8}Se$ thin films

$Cd_{1-x}Zn_xSe$ film	[hkl]	2θ (deg)	d (nm) Experimental	c (nm)	a (nm)	c/a (nm)
$Cd_{0.8}Zn_{0.2}Se$	(100) (002)	24.17 25.69	0.3682 0.347 (111)	0.693	0.425	1.631
$Cd_{0.6}Zn_{0.4}Se$	(100) (200)	24.87 26.51	0.358 0.337 (111)	0.682	0.413	1.651
$Cd_{0.4}Zn_{0.6}Se$	(100) (200)	26.59 28.33	0.335 0.319 (111)	0.671	0.392	1.711
$Cd_{0.2}Zn_{0.8}Se$	(100) (200)	26.95 28.49	0.331 0.311 (111)	0.658	0.384	1.713

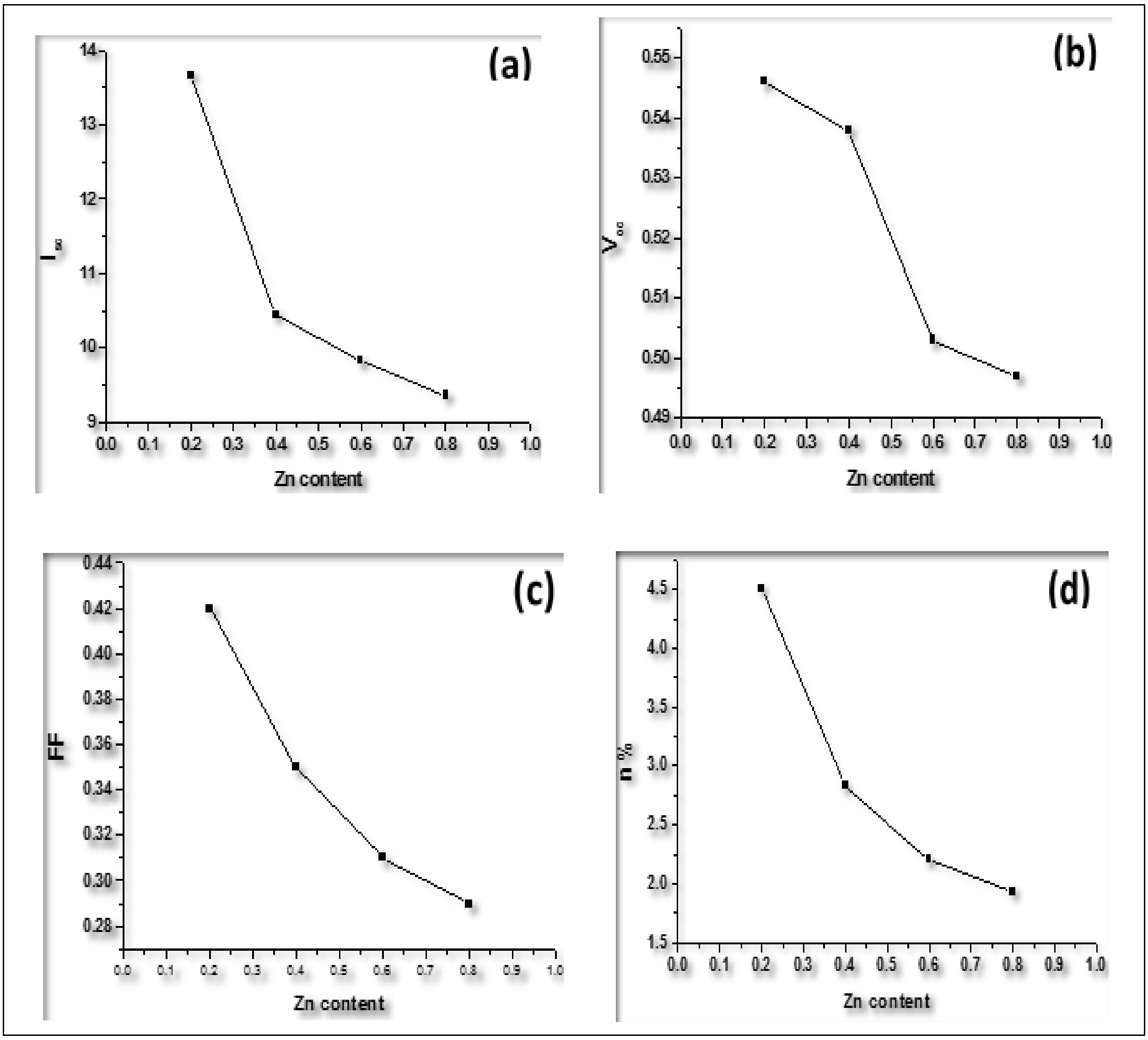

Fig. 5: Variation of PEC parameters: a) I_{SC} b) V_{OC} c) FF and d) η for $Cd_{1-x}Zn_xSe$ films with x = 0.2, 0.4, 0.6 and 0.8

4. CONCLUSION

PEC solar cells were fabricated using $Cd_{1-x}Zn_xSe$ films with various zinc content (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) incorporated into the starting CdSe film with nano-grain structure. The spectral response studies of these films have shown a gradual shift of optical absorption CdSe from about 1.90 to 2.92 eV with increased zinc content. The PEC solar cell output results have shown the conversion efficiency decreasing with increasing zinc content. The open-circuit voltage was increasing, but at the same time, the short-circuit current was decreasing with increasing zinc content. Such effects were attributed to the increased resistance and band gap values of Cd$_{1-x}$Zn$_x$Se films. It was observed that CdSe electrode modified with zinc content of $x = 0.2$ has delivered reasonably good output.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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