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Growth and Characterization of Electrochemically Deposited N-Cdse Thin Films for Photovoltaic Solar Cells

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ABSTRACT

Thin films of CdSe are deposited electrodeposition method and all preparative parameters are optimized properly to get good quality photovoltaic material. The XRD analysis reveals that the thin films of CdSe are polycrystalline in nature and the sharp peaks are identified as (111), (220), (400), and (331) planes of CdSe. The lattice constant 'a' was observed to be 6.042 Å, very close to the standard value of 6.0635 Å. The particle size is noted as 1.72 μm and 1.76 μm for CdSe films deposited on stainless steel and FTO coated glass substrates respectively. After annealing it is observed that the film annealed at 200°C indicates sharp peaks of maximum intensity. The average grain size of as deposited CdSe films is found as 0.45 μm and it increases to 0.5 μm after annealing. The EDAX study reveals that the as-formed and annealed films show the formation of CdSe material. After annealing more stoichiometric behaviour of the CdSe thin film is noted. The value of absorption coefficient is in the order of 10⁴ cm⁻¹ that supports the direct band gap nature with band energy 1.62 eV for the as-formed thin films and after annealing it decreases to 1.38 eV. The value of band gap energy shows the photovoltaic conversion span. The fill factor (FF) and power conversion efficiency (η) of the cell are 70 % and 4.48 % respectively. The negative polarity of dark voltage towards CdSe photo electrode and positive towards the graphite electrode for all samples showed n-type semiconducting behaviour.

KEYWORDS: Thin Films, XRD, EDAX, fill factor and efficiency.

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INTRODUCTION

For the last couple of decade's interest in the use of photoelectrochemical solar cells lead to large amount of research in the search for thin film polycrystalline materials with acceptable efficiency; sometimes approaching that of single crystals. Abundant literature is available on the preparation and characterization of semiconductor chalcogenide materials [1].

In recent years, thin films have attracted a great deal because of the different applications in the fields like semiconducting devices, photovoltaics, optoelectronic devices, radiation detectors, laser materials, thermoelectric devices, solar energy converters, etc.

CdSe is the one of promising materials because of its high absorption coefficient and the optimum band gap for the efficient absorption of solar radiation Photoelectrochemical studies of Indium doped CdSe thin films is carried out [2].The macrostructural and optical properties are studied[3]. The report on preparation of CdSe thin films by arrested precipitate method [4]. Effect of annealing on structural properties is studied [5]. Chemical Synthesis and the properties of CdSe films are studied and the nanocrystalline CdSe thin films are also deposited [6]. The effect Fe incorporation on properties of CdSe thin films is also reported [7].Effect of thickness on photoelectrochemical properties of CdSe is also studied [8]. The effect of Pb doping is also studied [9].

In the present work, electrochemical technique for depositing CdSe thin films is reported using a single parameter control of deposition potential. The effect of annealing on structural, optical, compositional, macrostructural and photoelectrochemical properties of electrodeposited CdSe thin films have been carried out by using XRD, optical absorption, EDAX, SEM and PEC techniques respectively.

EXPERIMENTAL:

The elementary depositions of Cd and Se were distinctly carried out at their respective concentrations and deposition potentials. The polarization curves for scrutinizing the deposition potentials were plotted for the plot of I Vs V (w.r.t SCE). Similarly electrodepositions of CdSe thin films were carried out with appropriate bath composition. The polarization curves were obtained for CdSe at various bath temperatures.

The pH of the electrolytic solution was kept at constant value by dilute H_2SO_4 .The preparative parameters such as growth time, pH of the bath and bath temperature were optimized by noting short circuit current (I_{sc}) and open circuit voltage (V_{oc}) of the PEC cell formed by the films deposited at various preparative parameters in order to get more photosensitive CdSe thin films.

The PEC cell was fabricated by using CdSe thin film as active photoelectrodes, polysulphide (0.1 M NaOH + 0.1 M Na₂S + 0.1 M S) solution as an electrolyte and graphite as a counter electrode was illuminated by 200 W tungsten filament lamp. The water compartment was inserted between the cell and lamp to avoid the direct heating of the cell. The films deposited at optimized preparative parameters were annealed at different temperatures. Annealing temperature was also optimized by PEC technique.

The as-deposited and annealed films were used for further characterization by XRD, optical absorption, EDAX, SEM and PEC techniques in order to study the structural, optical, compositional, and morphological and photoelectrochemical properties.

The X-ray diffraction patterns for CdSe thin films deposited onto stainless steel and FTO coated substrates were recorded by Philips X-ray diffractometer model 1710 with Cr-K α radiation in the span of angle between 10⁰ and 80⁰.

The optical absorption studies were carried using UV-VIS-IR spectrophotometer model Hitachi in the wavelength range 380 – 950 nm.

The surface morphology was studied by using JEOL, JXA – 840 reflection scanning electron microscopy using magnification of 10000 X at potential 20 kV with EDAX arrangement model.

The fill factor (ff) and power conversion efficiency (η) of the electrodeposited CdSe material were carried out by using above-mentioned PEC cell.

RESULTS AND DISCUSSION:

The deposition potentials for (CH₃COO)₂Cd₂H₂O (0.01M) was observed less as compared to deposition potential of SeO₂ (0.005M) and the deposition potential for (CH₃COO)₂Cd₂H₂O (0.01M, 10ml) + EDTA (0.01M, 5 ml) + SeO₂ (0.005M, 10 ml) is intermediate between (CH₃COO)₂Cd₂H₂O (0.01M) and SeO₂ (0.005M).

In order to optimize the deposition time the films were formed at various time intervals. The formula used is,

$$\text{Thickness} = \text{Mass formed} / (\text{density} \times \text{area})$$

$$t = \Delta M / (\rho \times A)$$

Where, ΔM = mass formed in gram. For that, the weight of the film was measured before and after the deposition. The plot of thickness Vs time is indicated in the Fig. 2. From this variation it is observed that, the thickness of film increases with deposition time and it becomes maximum for deposition time of 35 mins.

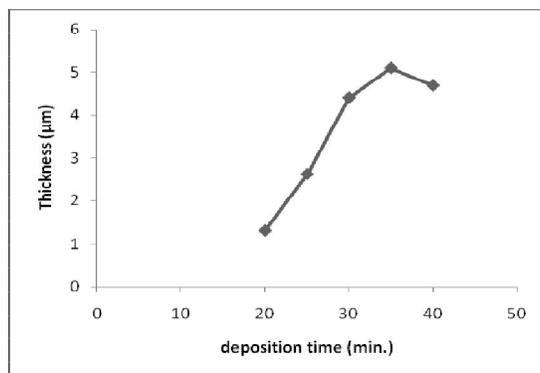


Fig.1. The plot of thickness Vs deposition time

From the Fig. 2, it is observed that I_{sc} and V_{oc} increases with bath temperature; become maximum at 60°C bath temperature and then decreases with further increase in bath temperature. The maximum value of I_{sc} and V_{oc} at particular bath temperature gives the optimized value of bath temperatures. The relatively higher value of I_{sc} can be attributed to shifting of the materials towards stoichiometry state. As we increase the bath temperature more and more thermal energy is supplied to the ions in the electrolytic solution and thus decreases the deposition potential of the material. As particular value of the temperature, the composition of the material formed is found stoichiometric giving good results of the PEC performance.

Fig. 3 the XRD patterns of CdSe thin films formed on stainless steel and annealed at 200°C . The XRD analysis reveals that the thin films of CdSe are polycrystalline in nature and the sharp peaks are identified as (111), (220), (400), and (331) planes of CdSe. The matching of observed 'd' values with standard ones depicted in Table 4.1, which confirms the creation of the CdSe material which is further confirmed by EDAX studies.

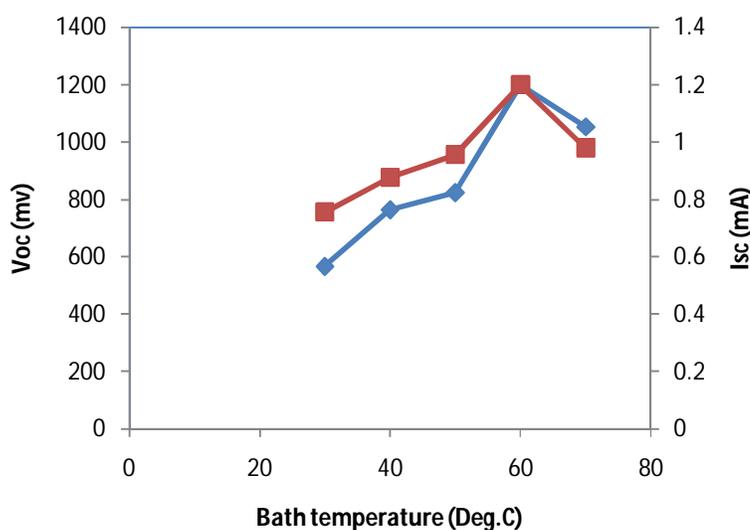


Fig.3 Variation of I_{sc} and V_{oc} with bath temperature

The lattice constant 'a' was observed to be 6.042 Å, very close to the standard value of 6.0635 Å as per ASTM data. After annealing it is observed that the peak intensity increases with increase in temperature and it is maximum at 200°C, after increasing temperature above 200°C, peak intensity decreases. Decrease in peak intensity may be due to deviation from stoichiometry of the materials at higher annealing temperature.

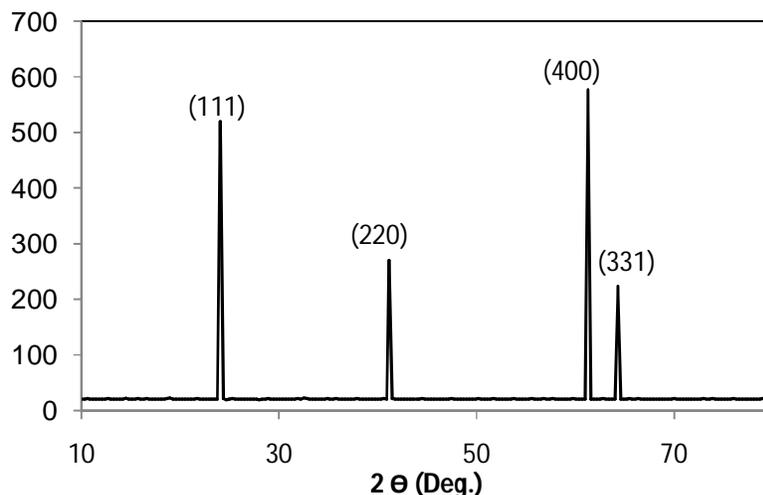


Fig.4. An X-ray diffractogram for the films annealed at 200°C.

The surface morphology of CdSe thin film formed at optimized preparative parameter is studied by Scanning Electron Microscopy (SEM). Fig. 5 indicates a surface morphology of the as formed and annealed film on surface of stainless steel substrate at 200°C respectively exhibiting its microstructure, the thin film of CdSe after annealing indicates smooth and uniform surface with a crack and pinhole free appearance with spherical shaped grains.

The surface morphology of CdSe thin film formed at optimized preparative parameter is studied by Scanning Electron Microscopy (SEM). Fig.5 indicates a surface morphology of the as formed and annealed film on surface of stainless steel substrate at 200°C respectively exhibiting its microstructure, the thin film of CdSe after annealing indicates smooth and uniform surface with a crack and pinhole free appearance with spherical shaped grains. After annealing improvement in grain alignment and surface continuity is observed. From these results it is concluded that the annealing of CdSe thin films formed on stainless steel and FTO coated glass substrate indicates improvement in surface morphology, results in to the improvement in photovoltaic characteristics due to decrease in its resistivity. The average grain size of as formed and annealed thin films is estimated and is indicated in table 1. From this it is depicted that after annealing grain size increases and this is the agreement with reports recorded by various researchers.

Table 1: The average grain size of as formed and annealed thin films.

Substrate	Grain Size (μm)	
	As-formed CdSe films	Annealed CdSe films at 200 $^{\circ}\text{C}$
SS	0.45	0.50
FTO	0.49	0.54

The compositional analysis of the as-formed and annealed thin films of CdSe at 200 $^{\circ}\text{C}$ is carried out by EDAX technique. The compositions for as-formed and annealed at 200 $^{\circ}\text{C}$ thin films are tabulated in table 1. The EDAX study reveals that the as-formed and annealed films show the creation of CdSe compound. After annealing more stoichiometric is noted, due to more stoichiometry of compound photovoltaic characteristics are improved. This result of compositional study supports the results obtained by earlier characterization methods. Fig.6 indicates the EDAX patterns of as formed and annealed films of CdSe on substrate of stainless steel.

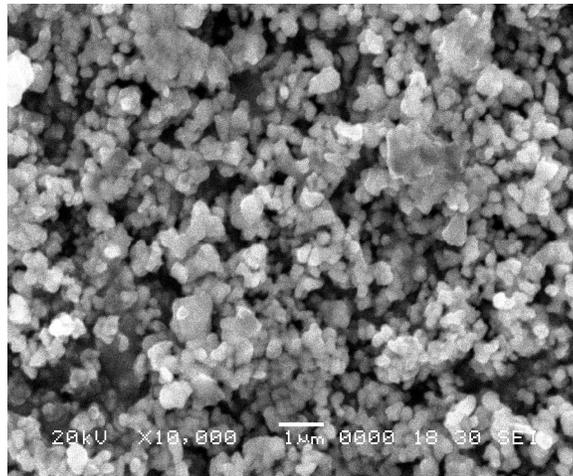


Fig.5. SEM picture of typical CdSe thin films

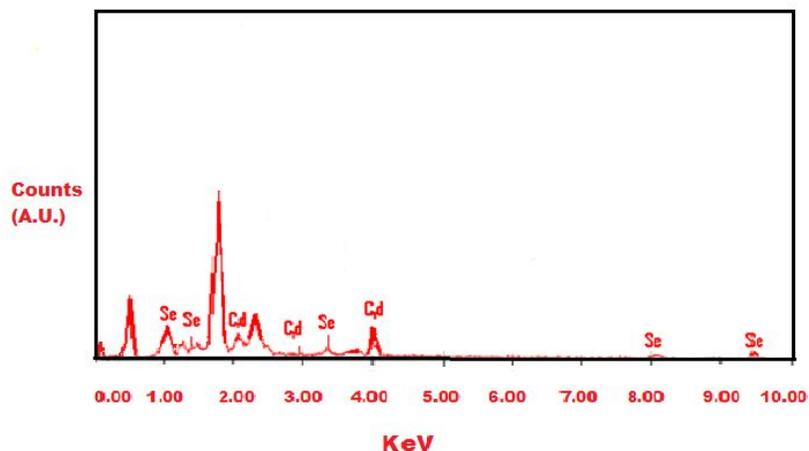


Fig.6.EDAX pattern of a typical CdSe thin film

The optical absorption of the as-formed and annealed CdSe thin films has been studied in the range 380 – 950 nm. The variation of optical density with wavelength is analysed to find out the nature of transition involved and the optical band gap.

The plot of $(\alpha h\nu)^2$ Vs. $h\nu$ for typical sample formed at optimized preparative parameters and annealed at 200^oC are indicated in Fig.7. The straight portions are indicating the presence of direct transition. The straight portions are extrapolated to energy axis at $\alpha = 0$, which gives the band gap energies of as-formed and annealed CdSe films to be 1.62 eV .Decrease in band gap after annealing may be due to more realignment in orientation leading to improved crystallinity and stoichiometry.

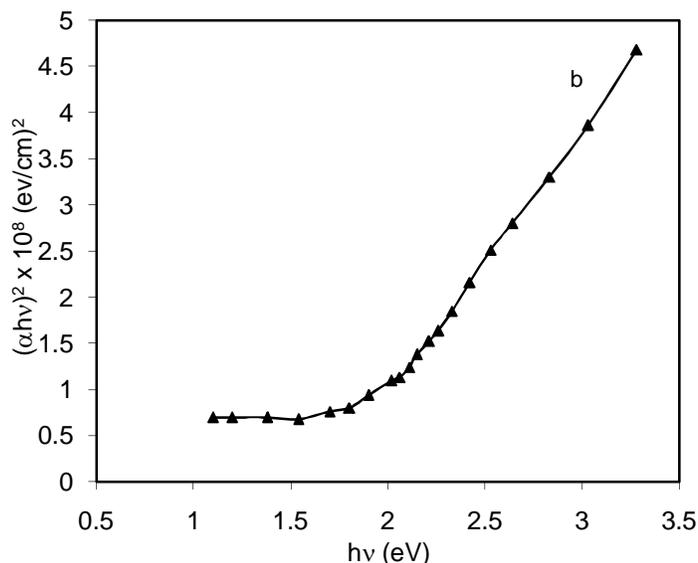


Fig.7.Variation of $(\alpha h\nu)^2$ Vs. $h\nu$ for typical CdSe thin films

Fig.8, indicates the photovoltaic power output characteristics for a typical cell (CdSe / 0.1 M NaOH + 0.1 M Na₂S + 0.1 M S / C) under the illumination intensity of 30 mW/cm² .The short circuit

current I_{sc} and open circuit voltage V_{oc} are found to be 2.8 mA and 480 mV respectively. The fill factor (ff) and power conversion efficiency (η) of the cell are 70 % and 4.48 % respectively.

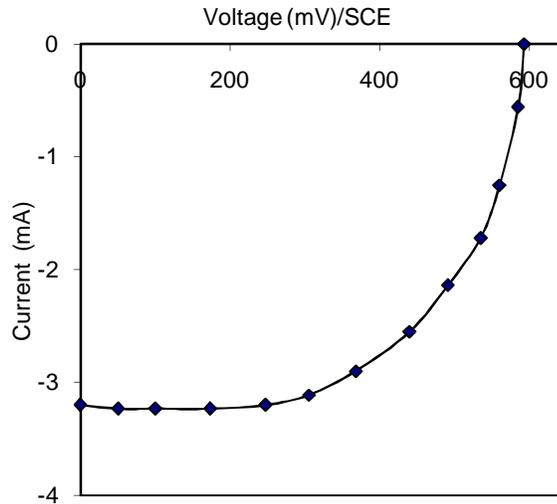


Fig. 8. The photovoltaic power output characteristics for a typical cell with CdSe

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