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Properties of Electrochemically Deposited CdTe Thin Films

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Abstract: Thin films of CdTe have been deposited on to stainless steel and fluorine doped tin oxide (FTO) coated glass substrates from aqueous acidic bath using electro deposition technique. The different preparative parameters, such as deposition time, bath temperature, pH of the bath have been optimized by photo electrochemical (PEC) technique in order to get good quality photosensitive material. The deposited films are annealed at different temperature in presence of air. Annealing temperature is also optimized by photo electrochemical (PEC) technique. The film annealed at 200^{O}C showed more photosensitivity. Different techniques have been used to characterize the as deposited and annealed (at 200^{O}C) CdTe thin film. The X-ray diffraction (XRD) analysis showed the polycrystalline nature and a significant increase in the XRD peak intensities is observed for the CdTe films after annealing. Optical absorption shows the presence of direct transition with band gap energy 1.64 eV and after annealing it decreases to 1.50 eV. Energy dispersive analysis by X-ray (EDAX) study for the as-deposited and annealed films showed nearly stoichiometric compound formation. Scanning electron microscopy (SEM) reveals that spherically shaped grains are more uniformly distributed over the surface of the substrate for the annealed CdTe film. Photovoltaic output characteristics and spectral response of the annealed film have been carried. The fill factor (ff) and power conversion efficiency (η) of the cell are found to be 71 % and 3.89 %.

Key words: PEC**,** XRD, band gap, EDAX, fill factor and efficiency.

INTRODUCTION

For the last couple of decades interest in the use of photo electrochemical 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- 9].

In recent years, thin films have attracted much interest because of their varied applications such as semiconducting devices, photovoltaics, optoelectronic devices, radiation detectors, laser materials, thermoelectric devices, solar energy converters, videcon devices, etc. [3-5, 10,11].

CdTe is a promising material because of its high absorption coefficient and the nearly optimum band gap for the efficient absorption of solar radiation. In the conventional solar cells, the wide band gap hetero-junction partner CdS is first deposited on the transport conducting glass substrate and the absorber layer CdTe is developed over the CdS layer [12-15]. CdTe films that have been grown onto very thin stainless steel, nickel and molybdenum substrates have been reported [16-19]. The electrical and optoelectronic properties of electrochemically deposited CdTe thin film are reported [20]. Structural and morphological properties of CdTe are reported by numbers of investigators [21,22]. Effect of electric field on spray deposited CdTe thin films are studied by Krishna et al [23]. Photo electrochemical characterization of CdTe in Nafion electrolyte is reported by Pantoja et al [24]. There are reports about the effect of the post-deposition heat treatment on the structural changes of CdTe thin films and its influence on the performance of CdTe based solar cells [25, 26].

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

EXPERIMENTAL

For CdTe deposition studies, 0.1M $CdSO_4$ was used as Cd source and TeO_2 as Te source, stainless steel and FTO coated glass substrates were used as cathode and graphite plate was as a reference electrode. De-ionised water of was used for the preparation of aqueous solution of the above precursor chemicals.

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 CdTe thin films.

The PEC cell was fabricated by using CdTe thin film as active photoelectrode, polysulphide (0.1 M NaOH + 0.1 M Na_2S + 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

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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, morphological and photo electrochemical properties.

The X-ray diffraction patterns for CdTe thin films deposited onto stainless steel and FTO coated substrates were recorded by Philips X-ray Diffractometer model 1710 with Cr-Kα radiation in the span of angle between 10^0 and 100^0.

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 5000 X at potential 20 kV with EDAX arrangement model.

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

RESULTS AND DISCUSSION

Thin films of CdTe are deposited at static potential mode to about 0.52 V with respect to SCE. Optimization of preparative parameters for deposition of good quality and stoichiometric CdTe thin films is most essential. Optimization of preparative parameters is carried out by noting the maximum values of I_{sc} and V_{oc} of the PEC cell. The fig.1 shows the variation Isc and Voc with deposition time, from the graph it is observed that Isc and Voc increases with increase in deposition time, attains maximum values for film deposited at 50 minutes and further increase in deposition time both Isc and Voc decreases this indicates that the formation of good quality and almost stoichiometric compound at 50 minutes. The lower values of Isc and Voc may be originated due to increase in resistivity of CdTe thin films deviated from stoichiometry [7,11]. The PEC cell with configuration CdTe / 0.1 M polysuphide / graphite is used to check the type of conductivity exhibited by CdTe thin films. The polarity of dark voltage is negative towards CdTe photoelectrode and positive towards the graphite electrode for all samples showing n–type semiconducting behavior. The fig.2 shows the variation of Isc and Voc with bath temperature. From the graph it is observed that Isc and Voc increases with increase in bath temperature and attains maximum values for the film deposited at 70°C, indicating probably a better formation of stoichiometric semiconducting compound, further increase in bath temperature, decreases the values of Isc and Voc. The lower values of Isc and Voc may be attributed to non-stoichiometric growth of CdTe thin films due to insufficient thermal energy provided during the deposition [11]. The fig.3 shows the variation Isc and Voc with pH of bath, which shows that Isc and Voc are maximum at pH = 3. This indicate that the formation of good quality photovoltaic material is possible from acidic aqueous bath [7]. Electrodeposition of CdTe films was carried out at potentiostatic mode at –520 mV / SCE. 1-2 μm thick layer was obtained within 50 min. of deposition time.

Annealing of the film (deposited at optimized preparative parameters) was done in air at four different temperatures 100, 150, 200, 250°C for 60 min. The fig.4 shows the variation Isc and Voc with annealing temperature, which shows that Isc and Voc are maximum for 200 °C annealing temperature. This may be due to heating at 200 °C in air produces more realignment in orientation leading to improved crystallinity and stoichiometry. Further increase in annealing temperature above 200 °C, Isc and Voc decreases this may be due to peeling off material from surface of substrate results deviation from stoichiometry in CdTe thin film. After annealing the CdTe samples showing p–type semiconducting behavior.

The XRD patterns shows the sharp peak reveals the polycrystalline nature of the as deposited CdTe films. The structural features fit into cubic one.

The XRD patterns for the as prepared and the annealed films at 200°C obtained are shown in fig.5 (a-b), respectively. Annealing at 200°C shows sharp intense peaks, which reveals that the films annealed at this temperature are more suitable for device application. A significant increase in the XRD peak intensities is observed for the CdTe film annealed at 200°C when compared to the peaks of as deposited sample. This reveals that the as deposited films were well crystallized and heating in air produces more realignment in orientation leading to improved crystallinity. The optical absorption of the as-deposited and annealed CdTe thin films has been studied in the range 380 – 950 nm. The variation of optical density with wavelength is analyzed to find out the nature of transition involved and the optical bandgap. The nature of the transition is determined by using the relation [7].

$$\alpha = A (h\upsilon - Eg)^n / h\upsilon \quad \text{--------- (1)}$$

where the symbols have their usual meanings.

For allowed direct transition, n = ½, the value of absorption coefficient is of the order of 10^4 cm^{-1} that supports the direct band gap nature of the semiconductor. The plot of $(\alpha h\upsilon)^2$ Vs. hυ for typical sample deposited at optimized preparative parameters (deposition time 50 min., bath temperature 70°C and at 3 pH) and annealed at 200^0C are shown in fig.6(a-b). The straight portions are indicating the presence of direct transition. The straight portions are extrapolated to energy axis at α = 0, which gives the band gap energies of as-deposited and annealed CdTe films to be 1.64 eV and 1.50 eV respectivley. Decrease in band gap after annealing may be due to more realignment in orientation leading to improved crystallinity and stoichiometry.

The compositional analysis for the as-deposited and annealed at 200^0C CdTe films are carried out by EDAX technique. The compositions for as-deposited and annealed (at 200°C) CdTe thin films are tabulated in table 1. EDAX study shows that the Cd to Te ratio is ~ 1 for as-deposited as well as annealed CdTe thin films.

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The surface morphology of CdTe thin film was studied by SEM picture. Fig.7(a-b) shows a surface morphology of the as deposited and annealed film at 200°C respectively exhibiting its microstructure, the film after annealing shows smooth and uniform surface with a crack and pinhole free appearance with spherical shaped grains.
The photoresponse of the PEC cell is measured by noting by noting Isc and Voc as a function of light intensity f_L. The equivalent diagram of PEC cell implies that Isc varies linearly with the light intensity as [27],

$$Isc = C.\, f_L \qquad \text{---------- (2)}$$

Where C is a constant. Variation of short circuit current Isc and open circuit voltage Voc as a function of light intensity for the PEC cell is depicted in fig.9. It is seen that Isc varies linearly over the whole range of light intensities under study. However, at higher intensities in Voc is observed which can be attributed to the saturation of the electrolyte interface charge transfer and nonequilibrium distribution of electrons and holes in the space charge region of the photoelectrode, which contribute a great deal to open cell photovoltage [27]. In case of solid junction, this deviation is attributed to the series resistance of the cell. The relation between Voc and light intensity for equilibrium distribution of the charge carriers in the space charge region is given by [28],

$$Voc = \text{constant} + (kT/q) \ln f_L - (kT/q) \ln (V_{oc}.q/\, kT) \qquad \text{.....(3)}$$

From fig.8, it is seen that the Voc saturates at a higher intensity, which is good agreement with the theory.

The plot of Isc against wavelength is shown in fig. 9. Isc attains maximum value at wavelength 817 nm and decreases with further increase of wavelength. The decrease of Isc on shorter wavelength side may be due to the absorption of light in the electrolyte and high surface recombination of photogenerated carriers by the surface states. The decrease in Isc on the longer wavelength side may be attributed to the non-optimized thickness and transition between defect levels [27,28]. The maximum Isc is obtained corresponding to wavelength 819 nm which gives the band gap 1.50 eV, agreeing with the result of optical absorption studies.

Fig.10 shows the photovoltaic power output characteristics for a typical cell (CdTe / 0.1 M NaOH + 0.1 M Na_2S + 0.1 M S / C) under the illumination intensity of 30 mW/cm^2 .The short circuit current Isc and open circuit voltage Voc are found to be 2.8 mA and 520 mV respectively. The fill factor (ff) and power conversion efficiency (η) of the cell are 72 % and 3.29 % respectively.

Table 1: Composition by EDAX for as deposited and annealed (at 200°C) CdTe thin films.

Element	Composition (at.%)	
	As deposited	Annealed at 200°C
Cd	52.63	48.32
Te	47.37	51.68

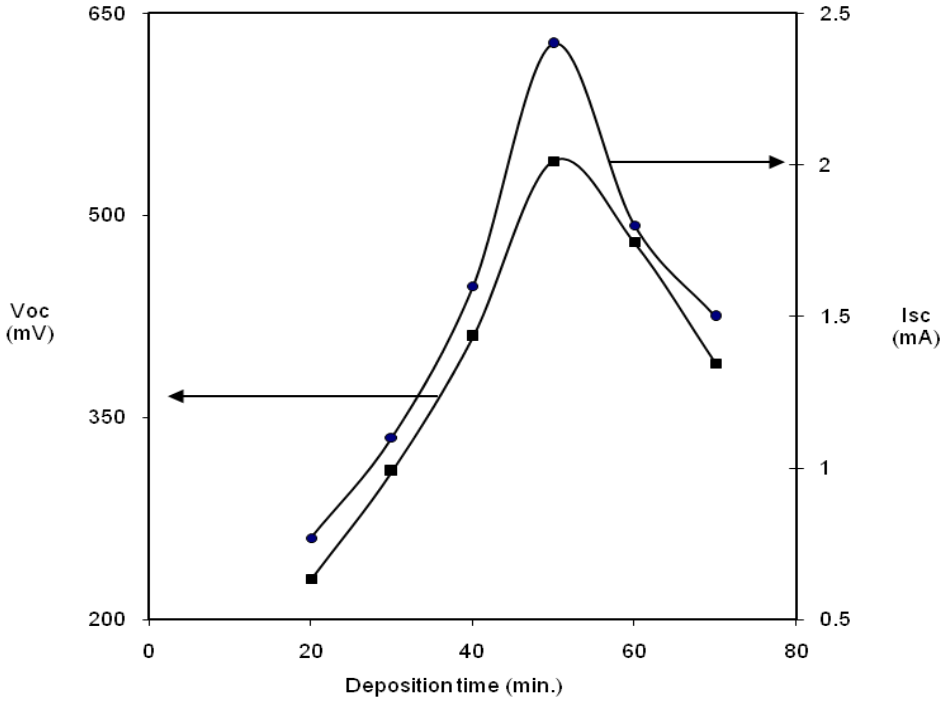

Fig.1: Variation of Isc and Voc with deposition time for the CdTe thin film.

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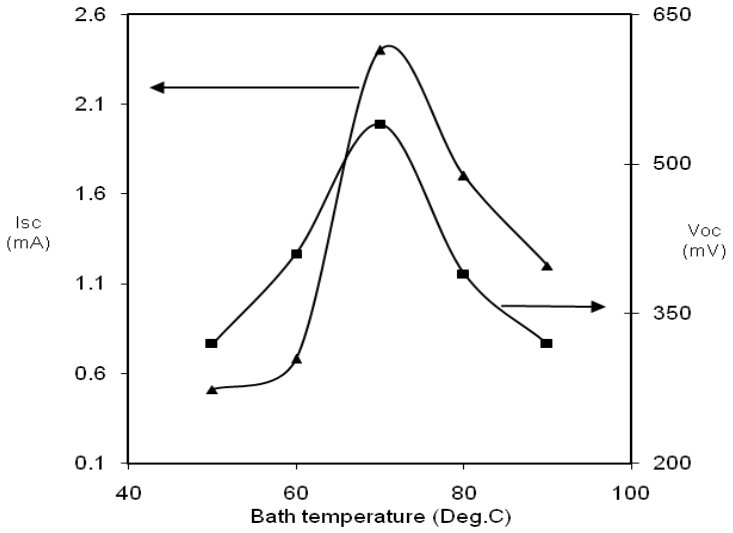

Fig.2: Variation of Isc and Voc with bath temperature for the CdTe thin film.

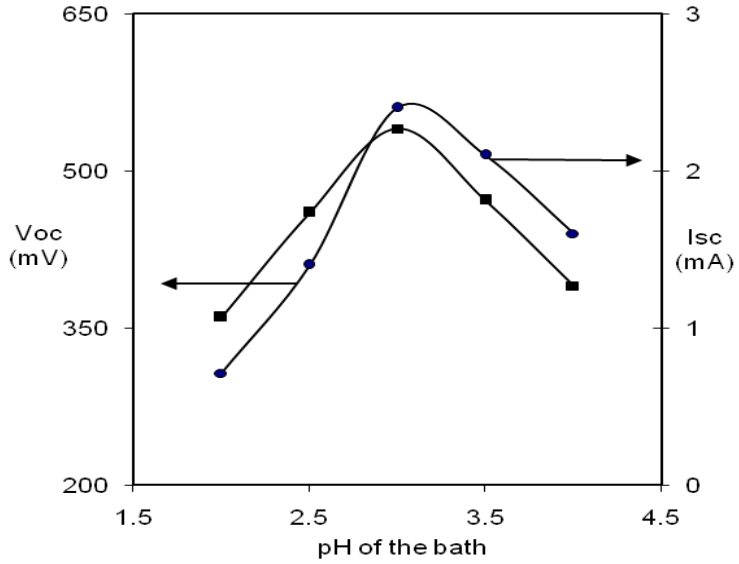

Fig.3: Variation of Isc and Voc with pH of the bath for the CdTe thin film.

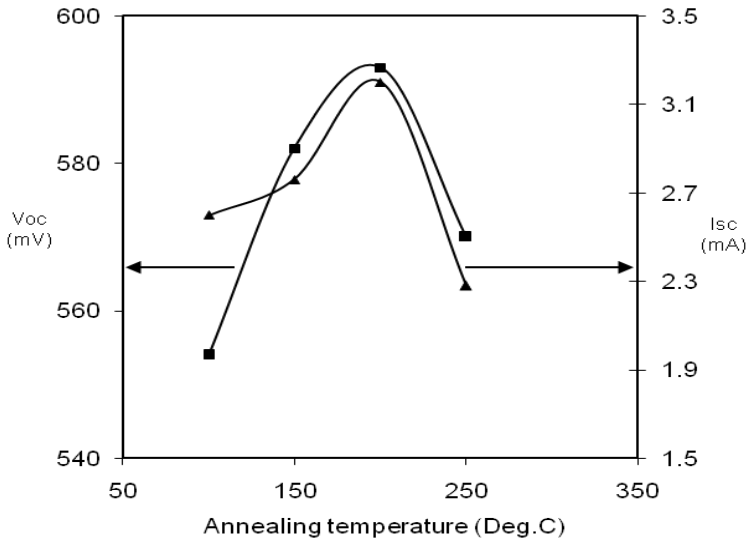

Fig.4: Variation of Isc and Voc with annealing temperature for the CdTe thin film.

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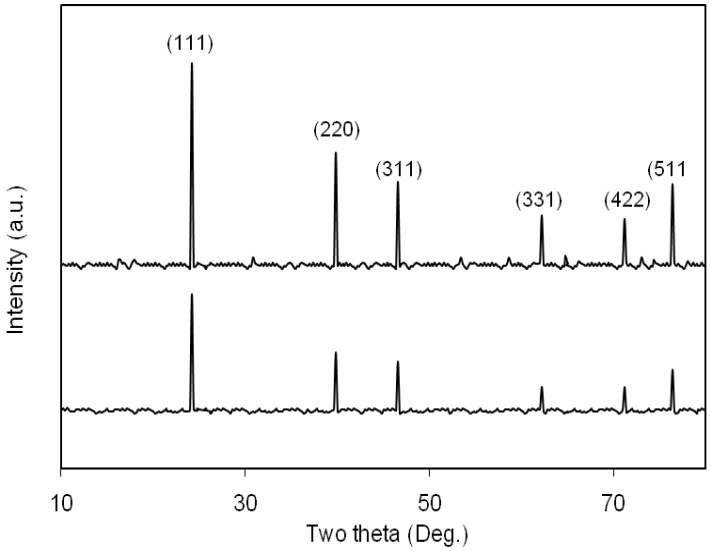

Fig.5: XRD pattern of CdTe a) as deposited b) annealed at 200°C

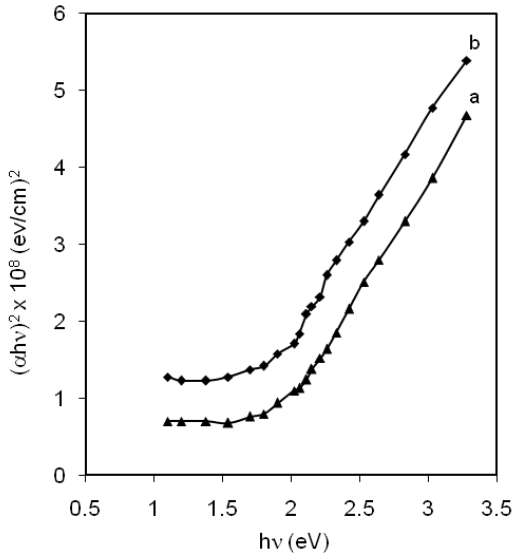

Fig.6 Variation of $(\alpha h\nu)^2$ Vs. hν for the CdTe thin films a) as deposited b) annealed at 200°C

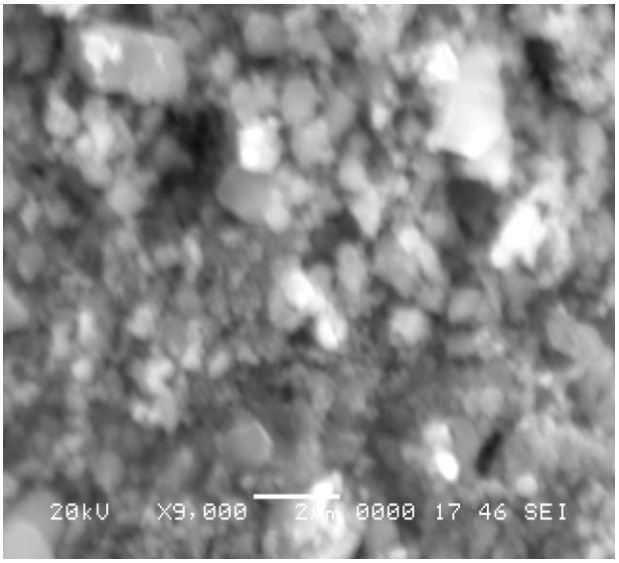

Fig.7: a: SEM picture for the as deposited CdTe thin film.

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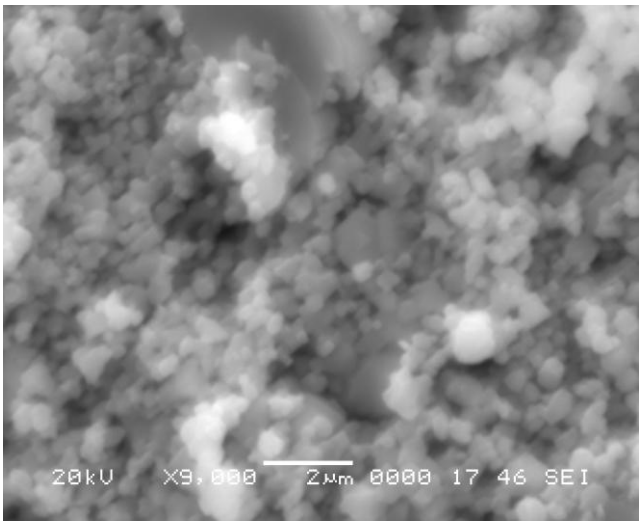

Fig.7 (b) SEM picture for the CdTe thin film annealed at 200oC.

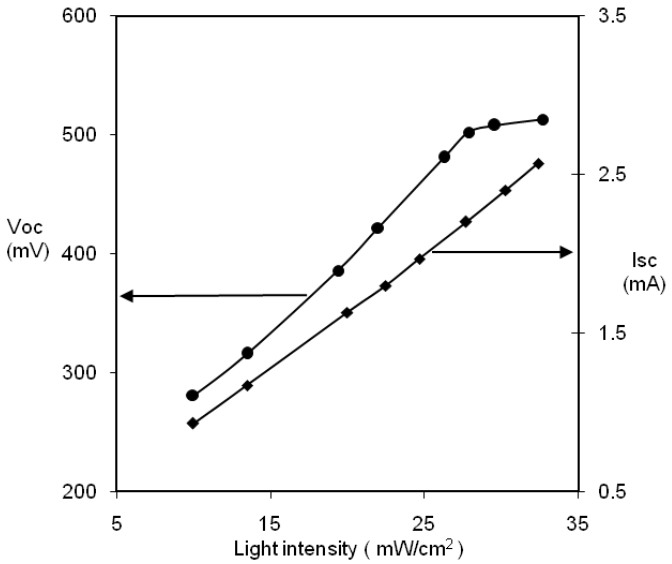

Fig.8: Variation of Isc and Voc with light intensity for the PEC cell formed with CdTe thin film (annealed at 200oC) as a photo anode.

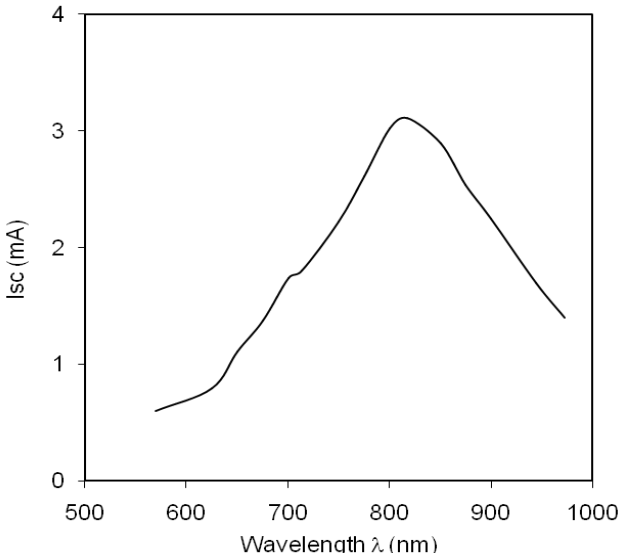

Fig.9. The plot of Isc against wavelength for CdTe thin films annealed at 200^{o}C

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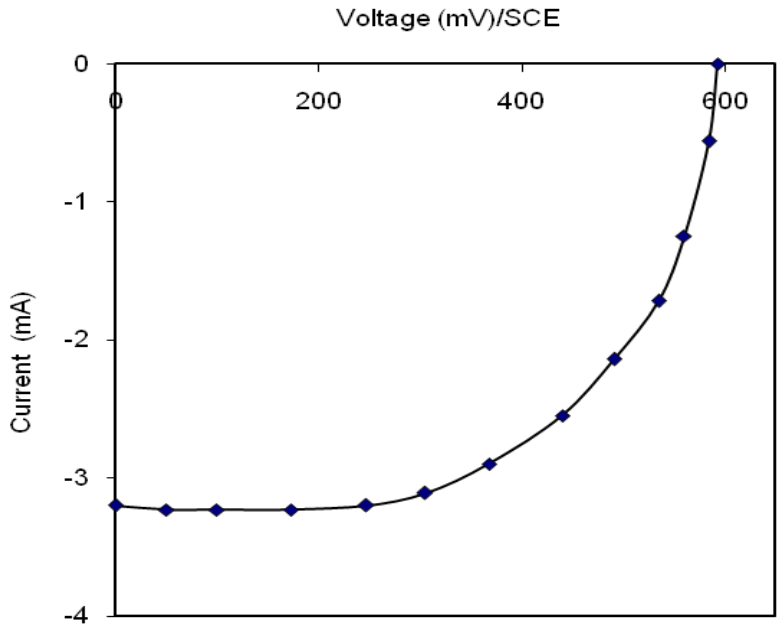

Fig.10: The photovoltaic power output characteristics for a typical cell with CdTe photoelectrode.

CONCLUSION

An electrochemical route for the preparation of CdTe thin films and effect of post annealing is studied. In order to prepare good quality deposits optimization of preparative parameters by PEC technique is suitable. The optical, compositional and morphological, analysis of as-deposited as well as annealed films has been carried out. The energy gap of the material is direct type with band gap energy (Eg) 1.64 and after annealing it decreases to 1.50 eV. Films prepared using the optimized deposition parameters show preferential orientation along (111) plane. Annealing treatment of the film in air shows an improvement in the polycrystalline nature of the film. From EDAX result Cd to Te ratio is almost found to be ~ 1. The SEM study shows that smooth and uniform growth of spherical shaped grains on surface substrate with a crack free appearance. The fill factor (ff) and power conversion efficiency (η) of the cell are 71 % and 3.89 % respectively.

REFERENCES

[1] S.K. Pandey, Umesh Tiwari, R. Raman, Chandra Prakash, Vamsi Krishna, Viresh Dutta and K. Zimik, Thin Solid Films, 473(2005) 54.
[2] Brian E. McCandless and Kevin D. Dobson, Solar Energy, 77(2004) 839.
[3] N.G.Patel, P.G.Patel, Solid State Electrochem. 35 (1992)1269.
[4] H.J.Goldsmid, J.E. Giutronich, M.M.Kalia, Solar Energy 24 (1980) 435.
[5] X.Mathew, P.J.Sebastian, Solar Energy Mater. Solar Cells 59 (1999) 85.
[6] X.Mathew, J.Phys. D: Appl. Phys. 33(2000) 1565.
[7] A.V.Kokate, U.B.Suryavanshi and C.H.Bhosale, J.Solar Energy 80(2006) 156.
[8] P.P.Hankare, S.D.Delekar, V.M.Bhuse, Chate P.A. and K.M.Garadkar, Semicond. Sci. Tech. 20(2005) 257.
[9] Y.Wada, S.Nishimatsu, J. Electrochem. Soc., 125 (1978) 1499.
[10] R.Chandramohan, T.Mahalingam, J.P.Chu, P.J. Sebastian, Solar Energy Mater. Solar Cells 81 (2004) 371.
[11] S.K.Deshmukh, A.V.Kokate and D.J.Sathe, Materials Sci.Engg. B 122 (2005) 206.
[12] Arturo Morales-Acevedo, Solar Energy Materials and Solar Cells 90, 6(2006)678.
[13] Jochen Van Gheluwe, Jorg Versluys, Dirk Poelman and Paul Clauws Thin Solid Films, 480(2005) 264.
[14] Javier Terrazas, Aaron Rodríguez, Cesar Lopez, Arev Escobedo, Franz J. Kuhlmann, John McClure and David Zubía, Thin Solid Films, 490(2005) 146.
[15] Steven S. Hegedus and Brian E. McCandless, Solar Energy Materials and Solar Cells, 88(2005)75.
[16] Rakhshani A.E.,J.Appl.Phys.81(1997) 7988.
[17] Singh V.P., McClure J.C., Lush G.B., Wang W., Wang X., Thompson G.W. and Clark E, Solar Energy Mater. Solar Cells, 59 (1999)59.
[18] Gamboa S.A., Sebastian P.J. and Rivera M.A., Solar Energy Mater. Solar Cells, 52(1998) 293.
[19] Rakhshani A.E., Makdisi Y. Mathew X and Mathew N.R., Phy.Stat.Sol.a 168 (1998).
[20] Xavier Mathew, J.Appl.Phys.,33 (2000)1565.
[21] S.Lalitha, R.Sathyamoorthy, S.Senthilarasu, A.Subbarayan and K. Natarajan, Solar Energy Materials and Solar Cells, 82(2004) 187.
[22] Joel Pantoja Enríquez and Xavier Mathew, Solar Energy Materials and Solar Cells, 81(2004)363.
[23] K. Vamsi Krishna, V. Dutta and P. D. Paulson, Thin Solid Films, 444 (2003)17.
[24] J. Pantoja, J. Moreira, P. J. Sebastián, X. Mathew and R. Castillo International Journal of Hydrogen Energy, (2003) 641.
[25] Joel Pantoja Enriquez and Xavier Mathew, Solar Energy Materials and Solar Cells, 81(2004)363. A. Romeo, D.L.Batzner, H.Zogg, A.N.Tiwari, Thin Solid Films, 361(2000) 420.
[26] J.D Desai and C.D.Lokhande, Mat.Chem.Phys,34(1993)313.
[27] V.V.Killedar, C.D.Lokhande and C.H.Bhosale, Indn. J. Pure Appl. Phy. 36(1998) 643.