



Trade Science Inc.

ISSN : 0974 - 7486

Volume 7 Issue 3

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(3), 2011 [146-151]

Concentration dependant structural and optical properties of spray deposited CdTe thin films

C.H.Bhosale*, D.M.Sapkal, V.M.Nikale, S.S.Shinde

Electrochemical Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, (INDIA)

E-mail : chb_phy@unishivaji.ac.in

Received: 15th November, 2010 ; Accepted: 25th November, 2010

ABSTRACT

Thin films of Cadmium Telluride have been deposited for various solution concentrations using a spray pyrolysis technique. The preparative parameters such as solution concentration, substrate temperature, quantity and pH of solution have been optimized using photoelectrochemical (PEC) technique. The PEC measurements show that both short circuit current (I_{sc}) and open circuit voltage (V_{oc}) are at their optimum values for the solution concentration of 10 mM at the optimized substrate temperature of 250°C. Further, the films have been characterized using X-ray diffraction (XRD), optical absorption, scanning electron microscopy (SEM), and energy dispersive analysis by X-ray (EDAX) techniques. XRD shows that the films are polycrystalline with cubic structure. The film deposited at optimized solution concentration has the well-formed grains as evidenced from SEM. EDAX analysis reveals that material formed is almost stoichiometric slightly rich in tellurium. The optical absorption studies confirm the existence of direct interband transition in CdTe with gap energy of 1.5 eV and absorption coefficient of the order of 10^4 cm^{-1} . © 2011 Trade Science Inc. - INDIA

KEYWORDS

Thin films;
Spray pyrolysis;
SEM;
X-ray diffraction;
Optical properties.

INTRODUCTION

Semiconducting materials have been receiving a great deal of interest among the researchers because of their potential applications in photovoltaic devices. Cadmium telluride is one of such semiconductors with applications such as photovoltaic cell, laser window, p-n diode, Gamma ray detector etc. The present status of CdTe thin film based solar cell includes 16% efficiency for devices on glass substrates^[1-3]. The CdTe is a member of II-VI photoconductive semiconductor of the type AX (A=Cd, Zn, Pb etc. and X= S, Se, Te

etc.) and has widely been studied^[4-7]. Among few semi-conducting materials, CdTe thin films are efficient photovoltaic energy converters due to their optimum direct band gap of 1.5 eV and high solar absorption^[8-11]. CdTe thin films can be prepared by a variety of techniques such as close spaced sublimation, spray pyrolysis, electrodeposition, thermal evaporation, screen-printing and sputtering. Among all these methods spray pyrolysis is a simple and low-cost technique, wherein the control of stoichiometry is obtained simply by varying the concentration of precursors and the substrate temperature. The deposition of II-VI semiconductor of sulfides and

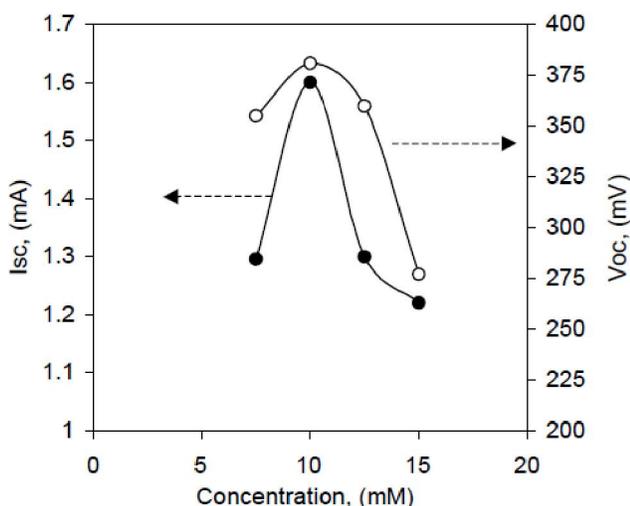


Figure 1 : Variation of I_{sc} and V_{oc} with solution concentration for CdTe thin film based polysulphide PEC solar cell

selenides by spray pyrolysis was first investigated by Chamberlin and Skarman^[12] and that of cadmium telluride films by Boone et al.^[8] and Jordan et al.^[13]. CdTe thin film can be electrodeposited from acidic^[14-16], basic^[17] and organic electrolytes^[18,19]. The Cd-chalcogenide thin film properties have been studied by others^[20-29].

This paper reports preparation of CdTe thin films onto the preheated glass substrates and fluorine doped tin oxide (FTO) coated glass substrates by a spray pyrolysis technique. The films have been characterized by photoelectrochemical (PEC), X-ray diffraction (XRD), optical absorption, scanning electron microscope (SEM) and energy dispersive analysis by X-ray (EDAX) techniques. A role of solution concentration on properties of spray deposited CdTe thin films have been studied.

EXPERIMENTAL

Preparation of CdTe thin films

CdTe thin films were deposited onto amorphous and fluorine doped tin oxide (FTO) coated glass substrates from a solution concentration of 7.5-15 mM by spray pyrolysis technique. TeO_2 was dissolved in hydrazine hydride, ammonium hydroxide and HCl, and finally mixed with aqueous solution of $CdCl_2$ to form a clear spraying solution with pH of 10.5. The solution was sprayed onto the preheated glass substrates maintained at substrate temperature of 250°C. Hydrazine

hydride used as a reducing agent to obtain Te^{2-} ions^[30].

The preparative parameters of CdTe thin films were optimized by varying the solution concentration at the fixed values of substrate temperature, quantity of spraying solution and pH value of solution. The solution pH value, quantity of solution, and spray rate were optimized to be 10.5, 30 ml and 1.5 cm^3/min respectively.

Characterization

The PEC cell consisted of CdTe thin film as an active photoelectrode, polysulphide solution (1 M NaOH + 1 M Na_2S + 1 M S) as an electrolyte and graphite as a counter electrode. The distance between photoelectrode and counter electrode was 0.5 cm. The cell was illuminated with 500 W tungsten filament lamp. The water lens was interposed between the lamp and the cell to avoid direct heating of the cell. The short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were measured with respect to various solution concentration. The structural characterization of the as-deposited CdTe thin films was carried out by analyzing the XRD patterns obtained using a Phillips X-ray diffractometer model PW 3710 based with Cr-radiation source having wavelength 2.2897 Å. Diffraction angle (2θ) in the XRD patterns varies from 10-100° with step width of 0.02°. The optical band gap was estimated from optical absorption measurement using a UV-VIS-NIR spectrophotometer (Hitachi model 330 Japan) in the wavelength range of 350-850 nm at room temperature.

The microstructural aspects were investigated by SEM model Cambridge Stereoscan 250-MK3 assembly and model XL-30 in series. The magnification used was 4000 X. The compositional analysis of the deposited material was carried out by EDAX attachment to above-mentioned SEM model.

RESULTS AND DISCUSSION

Deposition of CdTe thin films and effect of solution concentration on the film formation TeO_2 was added to a solution of ammonium hydroxide (NH_4OH), which was used as a solvent. TeO_2 takes 2-3 hours for its complete dissolution. Hydrazine hydrate ($N_2H_4 \cdot H_2O$) acts as a reducing agent for Te^{4+} ions and supplies six electrons to convert Te^{4+} to Te^{2-} ^[30]. Dilute HCl was

Full Paper

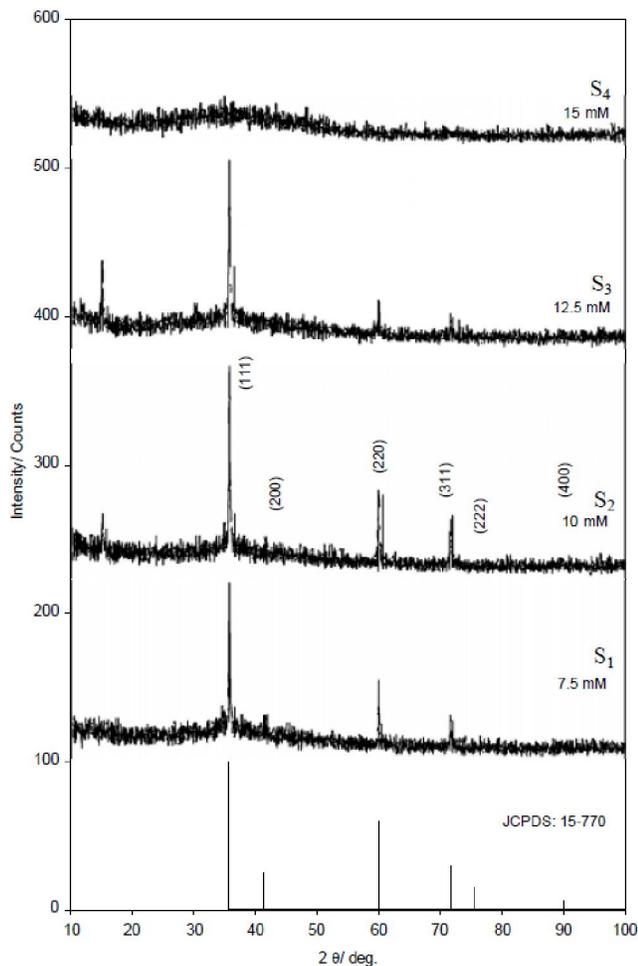


Figure 2 : X-ray diffraction patterns of the spray-deposited CdTe thin films obtained at different solution concentrations viz. 7.5, 10, 12.5 and 15 mM

also added at this stage, which shifts chemical equilibrium in the appropriate direction, thereby avoiding the precipitate formation at a later stage. The solution thus prepared was mixed with aqueous solution of CdCl_2 , which results in a slightly milky solution. Furthermore, the pH was well below the desired value required for preparing stoichiometric thin films. Hence by adding few more drops of NH_4OH , the pH was made to 10.5. Then this clear solution was used as the precursor. The solution was immediately sprayed onto the preheated glass substrates before formation of precipitate.

It has been observed that the mixing of CdCl_2 and TeO_2 solutions starts precipitating and complete precipitation occurs within half an hour. It is therefore essential to spray the mixed solution immediately after the mixing.

TABLE 1 : Variation of crystallite size with different solution concentrations at a fixed substrate temperature of 250°C

Solution concentration (mM)	Crystallite size (nm)
7.5	49.80
10	55.36
12.5	51.15
15	-

TABLE 2 : Observed and standard d values for the CdTe thin films at various solution concentrations $S_1=7.5$ mM, $S_2=10$ mM, $S_3=12.5$ mM, $S_4=15$ mM at fixed temperature 250°C

Standard	Observed d values (\AA) d				Reflection (hkl)
	S_1	S_2	S_3	S_4	
3.742	3.7415	3.7425	3.7415	-	(111)
3.270	3.2355	-	-	-	(200)
2.290	2.2906	2.2913	2.2918	-	(220)
1.954	1.9543	1.9557	1.9540	-	(311)

TABLE 3 : Elemental analysis of the spray-deposited CdTe thin film for the S_2 sample

Element	Wt %	At %	K-Ratio	Z	A	F
O K	15.82	32.98	0.054	1.1321	0.3016	1.0003
NaK	6.36	9.22	0.0273	1.0553	0.4052	1.0029
MgK	2.19	3	0.0118	1.0803	0.4982	1.0054
AlK	1.13	1.4	0.0073	1.0549	0.6102	1.01
SiK	36.09	42.85	0.282	1.0935	0.713	1.0023
CdL	14.51	4.31	0.1175	0.8349	0.9598	1.0101
TeL	23.9	6.25	0.1814	0.7884	0.9626	1
Total	100	100				

In the spray pyrolysis technique, the clear precursor solution was sprayed onto the preheated hot glass substrates and pyrolytic decomposition of solution occurs thereby resulting in well-adherent pale brown CdTe thin films. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic decomposition and breaks into its constituent components. The solvent and other volatile components get evaporated in the form of vapours and the only desired compound containing the Cd and Te chemical species deposit on the surface of substrate in thin film form.

The depositions of CdTe thin films were carried out at various solution concentrations 7.5, 10, 12.5 and 15 mM at the optimized substrate temperature of 250°C . It is seen that films prepared at solution concentration 15 mM are porous, nonuniform and not ad-

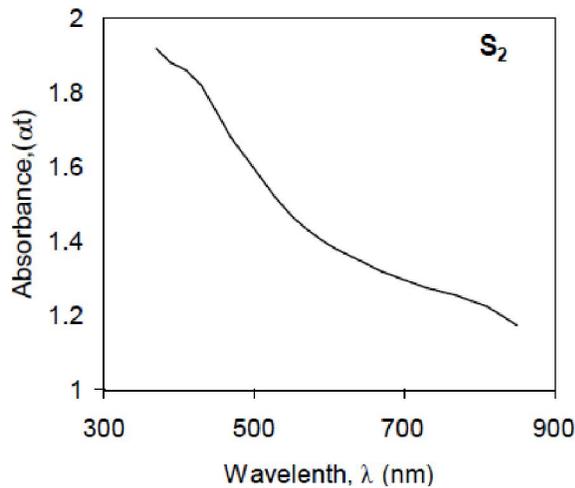


Figure 3 : Variation of absorbance (αt) with wavelength (λ) for the spray deposited CdTe thin film for the optimized solution concentration (S_2 sample)

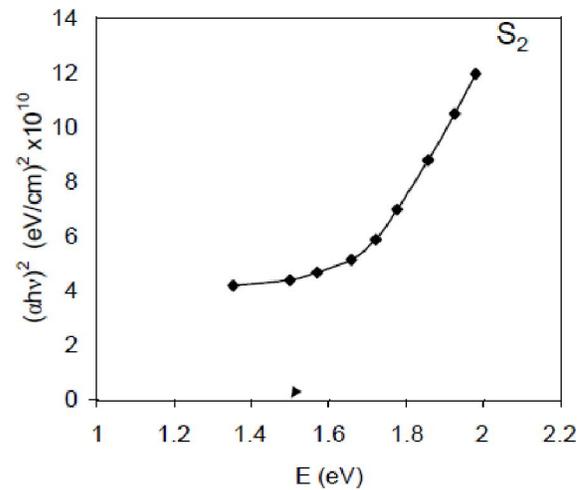


Figure 4 : Plot of $(\alpha hv)^2$ versus energy ($h\nu$) for the CdTe thin films deposited at optimized solution concentration (S_2 sample)

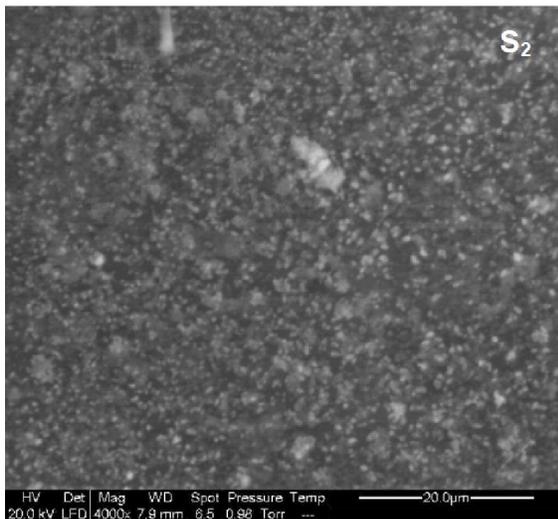


Figure 5 : Scanning electron micrographs of spray-deposited CdTe thin films at optimized solution concentration (S_2 sample)

herent to the substrates. The film formation does not observed below concentration 7.5 mM. This may be due to extra low concentration of the precursor solution. At higher concentration the complete thermal decomposition of the solution does not take place. However the CdTe thin films deposited at intermediate solution concentration (7.5-12.5 mM) are uniform and adherent to the glass substrates with faint brown in color.

Photoelectrochemical (PEC) studies

The quantities such as short circuit current (I_{SC}) and open circuit voltage (V_{OC}) of the PEC cell obtained with each CdTe thin film are observed to be relatively maxi-

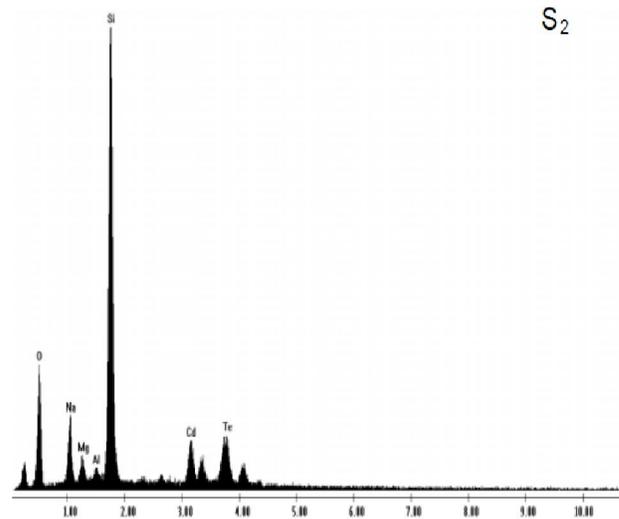


Figure 6 : Energy dispersive X-ray analysis (EDAX) of CdTe thin film deposited at optimized solution concentration (S_2 sample)

mum at optimized solution concentration of 10 mM as shown in figure 1. The relatively higher values of I_{SC} and V_{OC} at optimized solution concentration may be due to the observed more stoichiometry of the compound than that at other concentrations.

X-ray diffraction

Figure 2 shows the diffractograms obtained for CdTe thin films deposited at various solution concentrations on the glass substrates. The samples deposited from 7.5, 10, 12.5 and 15 mM solution concentrations are denoted as S_1 , S_2 , S_3 and S_4 respectively. It can be seen that the CdTe thin film samples obtained at solu-

Full Paper

tion concentration (7.5-12.5 mM) are polycrystalline. However the film becomes amorphous for solution concentration of 15 mM. The XRD pattern reveals that the concentration affects the growth mechanism of the films significantly. For the planes (111), (220) and (311) the crystallinity first increases reaches maximum at optimize solution concentration of 10 mM and again it decreases for solution concentration of 12.5 mM and it completely disappears for concentration of 15 mM. It reveals that it is amorphous in nature because substrate temperature is insufficient to supply the thermal energy for recrystallization and grain growth with increment in the solution concentration. Further decrease in crystallinity after 12.5 mM, may be attributed to the porosity, nonuniformity and nonstoichiometry of the as-deposited films.

In order to study crystallite size of CdTe particles, all the films were studied by taking a slow scan X-ray diffractometer. The crystallite size D can be obtained from

Debye Scherer equation for broadening due to particle size^[31,32].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where $k=0.9$, Q is the full width at the half maximum of a peak (FWHM), R is the diffraction angle and S is the wavelength of the X-ray radiation used (2.2897 Å).

TABLE 1 show that crystallite size is maximum around (111) plane at solution concentration of 10 mM. TABLE 2 confirms the 'd' values of the CdTe thin film calculated from the X-ray diffractograms with the standard 'd' values of the CdTe given in JCPDS data card^[33]. A matching the observed and the standard 'd' values confirms the film formation of compound CdTe with cubic crystal structure. The calculated value of lattice constant 'a' is found to be 6.48 Å agreeing well with the standard value for single crystal CdTe^[33,34].

Optical absorption studies

Optical absorption studies of the spray deposited CdTe thin films were carried out in the wavelength range 350-850 nm at room temperature. Figure 3 shows the variation of absorbance (Vt) with the wavelength (S). The absorption coefficient (V) for the films is found to be of the order of 10^4 cm^{-1} , supports the direct interband transition in the material. The nature of the

transition can be determined on the basis of dependence of absorption coefficient (V) on the photon energy ($h\nu$). Using the assumption that the transition probability becomes constant near the absorption edge, the absorption coefficient can be described as a function of photon energy^[35],

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (2)$$

where E_g is the band gap energy, $h\nu$ the photon energy, A is the constant and is a function of density of states near the conduction and valence band edges, with $n=1/2, 3/2, 2$ or 3 depending on whether the transition is direct allowed, direct forbidden, indirect allowed or indirect forbidden respectively.

Figure 4 shows variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for CdTe thin films. The plot exhibits almost linear variation towards the lower wavelength side and follows exponential behavior as wavelength increases further, thereby exhibiting a tail at the end. The exponential form of the tail can be ascribed to the existence of local impurities i.e. defects or disorder in the material. The optical band gap of CdTe material determined by extrapolating a straight portion of the energy axis at $V=0$ is 1.5 eV. The results are in good agreement with those reported by others^[6-9].

SEM and EDAX studies

Figure 5 shows the surface morphology of the spray-deposited CdTe thin films on glass substrates at optimized solution concentration of 10 mM and a fixed substrate temperature of 250°C. The micrograph reveals that the substrate is well covered with large number of densely packed grains. The compositional analysis of the CdTe thin films is carried out using EDAX technique for the films deposited at optimized solution concentration and the material is found to be slightly rich in Tellurium. The elemental analysis of CdTe thin films is shown in figure 6 and is tabulated in TABLE 3. The peaks other than Cd and Te are due to the elements present in the composition of glass substrate [Silica (SiO_2)+Na+Mg+Al].

CONCLUSIONS

CdTe thin film is possible using the spray pyrolysis technique. The films are polycrystalline in nature;

the crystallinity is maximum at the optimized solution concentration of 10 mM and the optical direct band gap energy is 1.5 eV. The concentration of precursor solution affects the structural and optical properties of CdTe thin films.

ACKNOWLEDGEMENT

Authors wish to thank the University Grants Commission, New Delhi for the financial assistance through the UGC-DRS-SAP II phase Project.

REFERENCES

- [1] J.Britt, C.Ferekides; *Appl.Phys.Lett.*, **62**, 2851 (1993).
- [2] S.Kumazawa, S.Shibutani, T.Nisho, T.Aramoto, H.Higuchi, T.Arita, A.Hanafusa, K.Omura, M.Murozono, H.Takakura; *Solar Energy Mater.Solar Cells*, **49**, 205 (1997).
- [3] T.Aramoto, S.Kumazawa, H.Higuchi, T.Arita, S.Shibutani, T.Nisho, J.Nakajima, T.Tsuji, A.Hanafusa, T.Hibino, K.Omura, M.Murozono; *Jpn.J.Appl.Phys.*, **36**, 6304 (1997).
- [4] M.Tomkiewicz, I.Ling, V.S.Parsons; *J.Electrochem.Soc.*, **129**, 2016 (1982).
- [5] C.Konigstein, M.Neumann-Spallart; *J.Electrochem.Soc.*, **145**(1), 337 (1998).
- [6] R.Chakrabarti, J.Datta, S.Bandopadhyaya, D.Bhattacharyya, C.Chaudhari, A.K.Pal; *Solar Energy Mater.Solar Cells*, **61**, 113 (2000).
- [7] R.K.Pandey, S.R.Kumar, A.J.N.Rooz, S.Chandra; *Thin Solid Films*, **200**, 1 (1991).
- [8] J.L.Boone, T.P.Van Doren, A.K.Berry; *Thin Solid Films*, **87**(3), 259 (1982).
- [9] P.C.Sarmah, A.Rehman; *Ind.J.Phys.A*, **64**, 21 (1990).
- [10] R.K.Sharma, Kiran Jain, A.C.Rastogi; *Current Appl.Phys.*, **3**, 199 (2003).
- [11] N.Romeo, V.Canevari, Zini, C.Spaggiari; *Thin Solid Films*, **157**, 175 (1988).
- [12] R.Chamberlin, H.Skarman; *J.Electrochem.Soc.*, **113**, 86 (1966).
- [13] J.F.Jordan, S.P.Albright; *Solar Cells*, **23**, 107 (1988).
- [14] B.M.Basol; *Solar Cells*, **23**, 69 (1988).
- [15] X.Mathew, P.J.Sebastian; *Solar Energy Mater.Solar Cells*, **59**, 85 (1999).
- [16] X.Mathew; *J.Phys.D.Appl.Phys.*, **33**, 1565 (2000).
- [17] G.F.Fulop, R.M.Taylor; *Ann.Rev.Mater.Sci.*, **15**, 197 (1985).
- [18] A.C.Rastogi, K.S.Balakrishnan; *J.Solar Energy Mater.Solar Cells*, **36**, 121 (1995).
- [19] K.S.Balakrishnan, A.C.Rastogi; *Solar Energy Mater.*, **23**, 61 (1991).
- [20] V.M.Nikale, N.S.Gaikwad, K.Y.Rajpure, C.H.Bhosale; *J.Mater.Chem.Phys.*, **78**, 363 (2002).
- [21] V.M.Nikale, C.H.Bhosale; *J.Solar Energy Mater.Solar Cells*, **82**, 3 (2004).
- [22] J.P.Enrquez, X.Mathew; *J.Cryst.Growth*, **259**, 215 (2003).
- [23] A.E.Rakhshani, Y.Makdisi, X.Mathew, N.R.Mathews; *Phys.Stat.Solar A*, **168**, 177 (1998).
- [24] X.Mathew, G.W.Thompson, V.P.Singh, J.C.McClure, S.Velumani, N.R.Mathews, P.J.Sebastian; *Solar Energy Mater.Solar Cells*, **76**, 293 (2003).
- [25] X.Mathew; *J.Mater.Sci.Lett.*, **21**, 529 (2002).
- [26] X.Mathew; *Solar Energy Mater.Solar Cells*, **76**, 225 (2003).
- [27] X.Mathew, P.J.Sebastian, A.Sanchez, J.Campos; *J.Solar Energy Mater.Solar Cells*, **59**, 99 (1999).
- [28] S.A.Gamboa, P.J.Sebastian, X.Mathew, H.Ngyen Cong, P.Chartier; *Solar Energy Mater.Solar Cells*, **59**, 115 (1999).
- [29] X.Mathew, J.P.Enriquez; *Solar Energy Mater.Solar Cells*, **63**, 347 (2000).
- [30] S.M.Kulify; *J.Amer.Chem.Soc.*, **83**, 4916 (1961).
- [31] C.S.Barrett, T.B.Massalski; In: 'Structure of Metals', 3rd Ed., Pergamon Press, Oxford, (1980).
- [32] H.P.Klug, L.U.Alexander; In: 'X-ray Diffraction Procedures', John Wiley and Sons, N.Y., (1974).
- [33] JCPDS Diffraction Data File No. 15-770, (1993).
- [34] K.Zanio; In: R.K.Willardson, A.C.Beer (Eds.); 'Semiconductors and Semimetals', Cadmium Telluride, 13, Academic Press, New York, (1978).
- [35] J.Herrero, C.Guillen; *J.Appl.Phys.*, **69**(1), 429 (1991).