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Effect of substrate temperature on the structural properties of spray deposited CdTe thin films

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ABSTRACT

The Cadmium Telluride (CdTe) thin films have been deposited onto the glass substrates using spray pyrolysis technique. The various preparative parameters such as substrate temperature, concentration, quantity and pH of solution have been optimized using photoelectrochemical (PEC) technique. Further, the films have been characterized using X-ray diffraction (XRD), optical absorption, Scanning electron microscopy (SEM), and Energy dispersive analysis by X-rays (EDAX) techniques. The PEC characterization shows that both short circuit current (I_{SC}) and open circuit voltage (V_{OC}) are at their optimum values for the optimized substrate temperature of 250°C and a solution concentration of 0.01 M. The XRD pattern shows that the films are polycrystalline with cubic structure. The optical absorption study reveals that CdTe exhibits a direct optical transition with band gap energy Eg to be 1.5 eV. The film at optimized temperature has well-formed grains as evidenced from SEM. The EDAX analysis reveals that material formed is almost stoichiometric at optimized preparative parameters.

KEYWORDS

Thin films;
Chemical synthesis;
Electron microscopy;
X-ray diffraction;
Optical properties.

INTRODUCTION

Cadmium telluride is a one of the II-VI compound semiconductors and is a potential candidate as a photovoltaic material because of its optimum band gap of (~1.5 eV) and high absorption coefficient in the visible region[1,2]. It has many applications such as photovoltaic cells, laser window, p-n diode, Gamma ray detector etc[2-5]. The deposition of II-VI semiconductor sulphides and selenides by spray pyrolysis was first investigated by Chamberlin and Skarman[6], and that of cadmium telluride films by Boone et al.[7] and Jordan et al.[8].

Rastogy and Balkrishnan[9] studied electrodeposited CdTe films for their growth structure and composition. R. F. Sputtered n-CdTe film has been used to fabricate Schottky barrier junction with Ag metal[10]. K. Vamshi et al.[11] have reported the effect of electric field on CdTe thin films deposited using spray pyrolysis. The chemical spray pyrolysis is a technique for depositing polycrystalline films of oxides, binary and ternary chalcogenides, and superconducting oxide thin films[12]. The II-VI compound semiconductors of the type AX (A= Cd, Zn, Pb etc. and X= S, Se, Te etc.) have widely been studied[13-16]. The properties of Cd-chalcogenide thin films have been studied by other investigators[17-26].

The present study deals with the preparation of CdTe thin films at various substrate temperatures on preheated glass substrates by a simple and low-cost spray pyrolysis technique. The films have been characterized by photoelectrochemical (PEC), X-ray diffraction (XRD), optical absorption, scanning electron microscopy (SEM) and energy dispersive analysis by X-rays (EDAX) techniques and results have been discussed.

EXPERIMENTAL

Preparation of CdTe thin films

The thin films CdTe were deposited onto a bare glass and the fluorine doped tin oxide (FTO) coated glass substrates at different substrate temperatures. The precursor solution to be sprayed was prepared by appropriate volumetric proportion of aqueous cadmium chloride ($CdCl_2$) and Tellurium dioxide (TeO_2) dissolved in hydrazine hydride, NH_4OH and HCl being used to form clear spraying solution with optimized pH value. Hydrazine hydride served as a reducing agent to obtain Te_2- ions[27]. The pH, concentration and the spray rate of the precursor solution were optimized to be 10.5,

0.01 M and 1.5 ml min^{-1} respectively. The films were deposited at various substrate temperatures from 225 to 300°C at the interval of 25°C in order to obtain good quality, stoichiometric and uniform CdTe thin films.

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 short circuit current (Isc) and open circuit voltage (Voc) were measured with respect to the substrate temperature for optimizing the preparative parameters. The structural analysis of the as-deposited CdTe thin films was carried out by using a Phillips x-ray diffractometer model PW 3710 using Cr-radiation source having wavelength 2.2897 Å. X-ray diffraction patterns of the films were recorded by varying diffraction angle (2θ from 10-100° with step width of 0.02°. The optical absorption studies were carried out using a UV-VIS-NIR spectrophotometer (Hitachi model 330 Japan) in the wavelength range of 350-850 nm at room temperature.

The surface morphology of the spray-deposited CdTe thin films on glass substrate was carried by SEM model Cambridge Stereoscan 250-MK3 assembly and model XL-30 in series with 4000 X magnification. The compositional analysis of the film was studied by the EDAX attachment to above-mentioned SEM model.

RESULTS AND DISCUSSION

Deposition of CdTe thin films and effect of substrate temperature 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 few hours for complete dissolution. Hydrazine hydrate ($N_2H_4.H_2O$) acts as a reducing agent for Te_4+ ions and supplies six electrons to convert Te_4+ to Te_2-. Dilute HCl was also added at this stage, which shifts chemical equilibrium in the appropriate direction, thereby avoiding the precipitate formation at a later stage. Solution thus prepared was mixed with aqueous solution of CdTe, which resulted in a slightly milky solution. Furthermore, the pH was well below the desired value required for preparing stoichiometric thin films. Hence the pH was increased by adding few more drops of NH_4OH. Then this clear solution was used as the precursor. The solution was immediately sprayed onto the preheated glass substrates before formation of precipitate.

In the spray pyrolysis technique, the clear precursor solution of CdTe was sprayed onto the preheated hot glass substrates, 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 evaporate in the form of vapors and the only desired compound containing the required chemical species deposits on the surface of substrate in thin film form.

The depositions of CdTe thin films were carried out at various substrate temperatures in the range 225-300°C using 0.01 M solution. It was observed that the lower substrate temperatures (<225°C) favor non-uniform and easily detachable film formation. The temperature might be insufficient in this case, to decom-

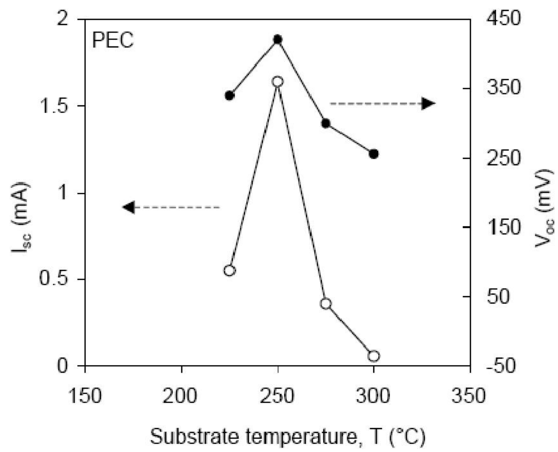

Figure 1 : Variation of Isc and Voc with substrate temperature for CdTe thin film based polysulphide PEC solar cell

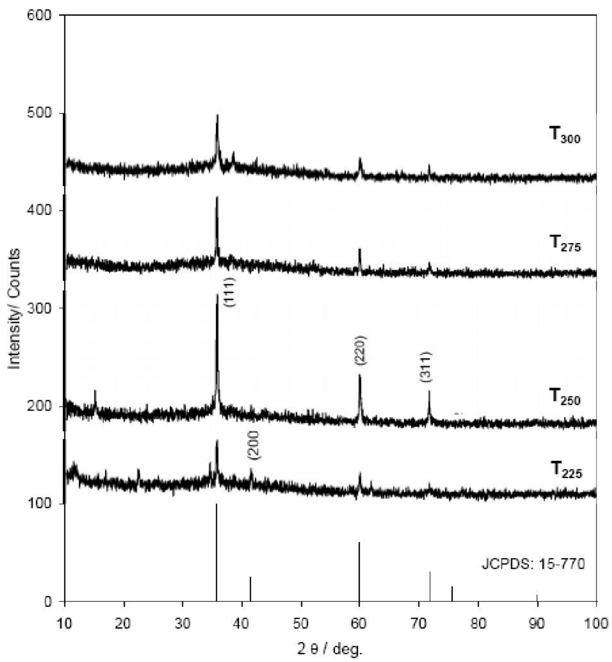

Figure 2 : X-ray diffraction patterns of the spray-deposited CdTe thin films obtained at different substrate temperatures viz. 225, 250, 275 and 300°C

pose the sprayed droplets of the mixed solution. At higher substrate temperatures (>300°C) also the films resulted with nonuniformity and pinholes. This could be due to the higher evaporation rate of the initial ingredients from the surface of the hot substrates. However the CdTe thin films deposited at intermediate substrate temperatures are uniform and adherent to the glass substrates. The films are faint brown in colour.

Photoelectrochemical (PEC) studies

The quantities such as short circuit current (Isc) and

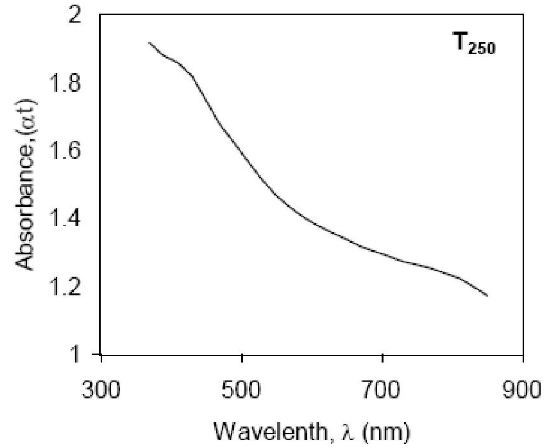

Figure 3 : Variation of optical absorbance (αt) with wavelength (λ) for the spray deposited CdTe thin film for the optimized substrate temperature (T250 sample)

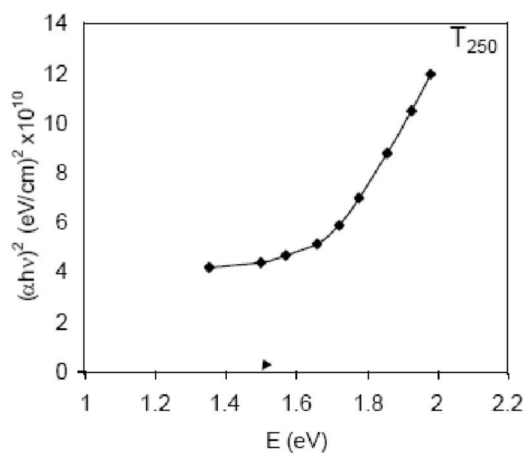

Figure 4 : Plot of (αhυ)2 versus energy (hυ) for the CdTe thin films deposited at optimized substrate temperature (T250)

open circuit voltage (Voc) of the PEC cell obtained with each CdTe thin film are observed to be comparatively maximum at optimized substrate temperature of 250°C as shown in figure 1. The comparatively higher values of Isc and Voc at optimized substrate temperature may be due to the relatively maximum stoichiometry of the compound at that temperature.

X-ray diffraction

Figure 2 shows the diffractograms obtained for CdTe thin films deposited at various substrate temperatures on the glass substrates. The samples deposited at 225, 250, 275 and 300°C, are denoted as T225, T250, T275 and T300 respectively. The (111), (220) and (311) are among the prominent reflections that occurred for the T250 sample. The deposits are found to be polycrystalline in nature. It can be seen from the

TABLE 1 : Observed and standard *d* values for the CdTe thin films at various substrates temperatures

Sr. No.	Standard d values (Å)	Observed d values (Å)				Reflections (hkl)
		T_{225}	T_{250}	T_{275}	T_{300}	
1	3.742	3.7415	3.7425	3.7441	3.7410	(111)
2	3.270	3.2269	-	-	-	(200)
3	2.290	2.2904	2.2913	2.2951	2.2872	(220)
4	1.954	1.9538	1.9557	1.9561	1.9554	(311)

TABLE 2 : Elemental analysis of the spray-deposited CdTe thin film for the T_{250} sample

Element	Wt %	At %	K-Ratio	Z	A	F
OK	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				

diffractograms that highest peak intensity is associated with the (111) plane.

TABLE 1 compares the d values of the CdTe thin films calculated from the X-ray diffractograms with the standard ones of the CdTe given in the JCPDS data card[28]. A matching of the observed and the standard d values confirms the film formation of compound CdTe with cubic crystal structure as reported by S.R. Vishwakarma[17]. The calculated value of lattice constant (a) is found to be 6.484 Å agreeing well with the standard value for single crystal CdTe[28,29]. It reveals that as the substrate temperature increases, crystallanity also increases. Relatively higher peak intensity has been observed for the CdTe thin films deposited at 250°C. The XRD peak intensity decreases towards the higher substrate temperature (>250°C). This could be due to the sufficient increase in supply of thermal energy for the recrystallization and grain growth with increment in the substrate temperature. Further decrease in crystallanity after 250°C may be attributed to the non-uniformity of the as-deposited films.

Optical absorption studies

The optical absorption spectra of the as-deposited films were recorded in the wavelength range of 350-850 nm at room temperature. Figure 3 shows the variation of absorbance (αt) with the wavelength (λ). It reveals that optical absorption coefficient (α) is a function of photon energy.

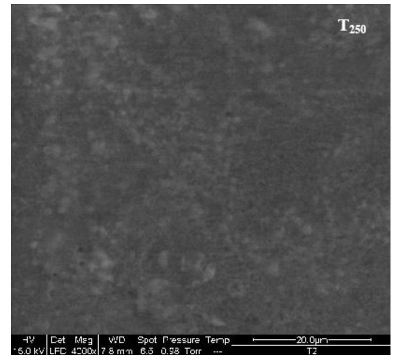

Figure 5 : Scanning electron micrographs of spray-deposited CdTe thin films at optimized substrate temperature (T250)

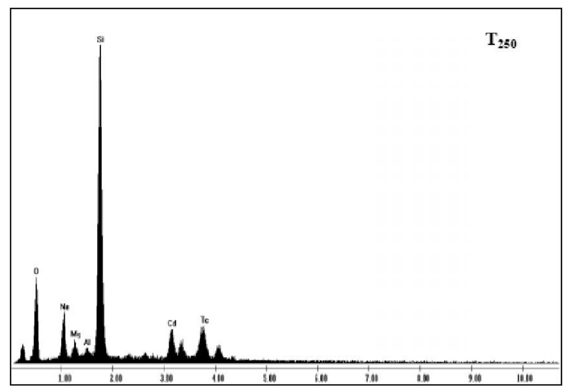

Figure 6 : Energy dispersive x-ray analysis (EDAX) of CdTe thin film deposited at optimized substrate temperature (T250)

$$\alpha = \frac{\alpha_o (h\nu - E_g)^n}{h\nu} \qquad (1)$$

It also shows higher absorption towards the shorter wavelength side and the presence of an absorption edge. The optical interband transition in the semiconductor is governed a well-known relation[30] given by, where Eg is the band gap energy, hυ the photon energy, αo is the constant and is a function of density of states near the conduction and valence band edges, with n being ½ and 2 for direct and indirect optical transition.

Figure 4 shows variation of $(\alpha h\upsilon)_2$ versus hυ. 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 α=0 is 1.5 eV. The results are in good agreement with those reported by others[1,7].

SEM and EDAX studies

Figure 5 shows the surface morphology of the spray-deposited CdTe thin films on glass substrates at optimized substrate temperature of 250°C. The micrograph reveals that the substrate is well covered with large number of densely packed more-or-less spherical grains. The compositional analysis of the CdTe thin films is carried out using EDAX technique for the films deposited at optimized substrate temperature. 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]. The material is found to be nearly stoichiometric. The elemental analysis of CdTe thin films is shown in figure 6 and is tabulated in TABLE 2.

CONCLUSIONS

The deposition of semiconducting CdTe by spray pyrolysis technique is feasible. The films deposited at optimized substrate temperature (250°C) and concentration (0.01 M), are polycrystalline and stoichiometric with cubic structure exhibiting good photovoltaic activity.

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