Physical properties of spray deposited CdTe thin films: PEC performance

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Abstract: p-CdTe thin films were prepared by spray pyrolysis under different ambient conditions and characterized using photoelectrochemical (PEC), X-ray diffraction (XRD), scanning electron microscopy, energy-dispersive analysis by X-ray (EDAX), and optical transmission studies. The different preparative parameters viz solution pH, solution quantity, substrate temperature and solution concentration have been optimized by the PEC technique in order to get good-quality photosensitive material. XRD analysis shows the polycrystalline nature of the film, having cubic structure with strong (111) orientation. Micrographs reveal that grains are uniformly distributed over the surface of the substrate indicating the well-defined growth of polycrystalline CdTe thin film. The EDAX study for the sample deposited at optimized preparative parameters shows the nearly stoichiometric Cd : Te ratio. Optical absorption shows the presence of direct transition with band gap energy of 1.5 eV. Deposited films exhibit the highest photocurrent of 2.3 mA, a photovoltage of 462 mV, a 0.48 fill factor and 3.4% efficiency for the optimized preparative parameters.

Key words: CdTe; PEC; temperature; concentration; structure; morphology; composition; optical

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1. Introduction

Cadmium telluride is one of the most promising II–VI semiconductor compounds for many electronic and optoelectronic devices because of its optical and transport properties. The high absorption coefficient ($> 10^4$ cm^{-1}) of the material in the visible and near IR region of the solar spectrum and the direct band gap close to the optimum value (ca. 1.5 eV) for efficient solar energy conversion make it ideal for solar cell fabrication[1]. Good quality CdTe thin films have wide applications, such as γ-ray detectors, infrared windows, solar cells, and other optoelectronic devices[1]. Currently, the material is receiving renewed interest due to the search for cheaper technologies for the mass production of solar cells that do not require high quality monocrystals. The deposition methods and preparation conditions for the fabrication of CdTe are very important for the achievement of high solar cell conversion efficiency[2]. Several thin film deposition techniques viz. electrodeposition[3], closed-space sublimation CSS[4], spray pyrolysis[5], physical vapor deposition, vacuum evaporation, vapor transport deposition, closed space vapor transport, screen printing, MOCVD and RF sputtering[6–8] have been used to obtain photovoltaic quality p-CdTe films, which with an n-type CdS window layer have yielded solar cells with a conversion efficiency of up to 16%[9]. One of the critical stages in thin film solar cell fabrication is the deposition of a CdTe layer with controllable composition and stoichiometry. It has been pointed out that high efficiency solar cells possess Te-rich CdTe surfaces with smooth interfaces of p-CdTe/n-CdS[10]. Chemical spray pyrolysis can be one of the techniques, which may be more suitable for this purpose. A big advantage is that, in this technique, the properties of the thin films can easily be changed by varying the deposition conditions. It is a low equipment cost technique for depositing thin polycrystalline films of oxides, binary and ternary chalcogenides and superconducting oxide films[12]. Seth *et al.*[4] studied the growth and characterization of CdTe by close spaced sublimation on metal substrates using light-weight molybdenum foils as the precursor. Ison *et al.*[5] studied the synthesis and characterization of spray deposited CdTe films grown under different ambient conditions. They confirmed the role of spray ambient by preparing samples over a range of ambient conditions that resulted in the formation of CdTe films with and without oxide phases. Razykov *et al.*[8] reported that the CdTe films with different compositions (Cd-rich, Te-rich and stoichiometric) were fabricated by a novel and low cost chemical molecular beam deposition method (CMBD) in atmospheric pressure hydrogen flow using Cd and Te granules as precursors on to the ceramic substrates. Chapman *et al.*[13] investigated microstructural changes of CdTe during the annealing process deposited by a physical vapour deposition technique. Higher CdTe deposition rates correlated to increased Te concentration for the as-deposited films decreased significantly during annealing.

The present paper reports the synthesis and characterization of stoichiometric p-CdTe thin films using a simple and low cost spray pyrolysis technique onto the amorphous and fluorine doped tin oxide coated conducting glass substrates. The effect of different ambient conditions, such as solution pH, solution quantity, substrate temperature and solution concentration, on the photoelectrochemical, structural, microstructural, compositional and optical properties have been investigated by PEC, X-ray diffraction, scanning electron microscopy, energy dispersive analysis by X-rays and optical absorption techniques, respectively. Variation in the dislocation density, strain and texture coefficient w.r.t. the substrate temperature and concentration has been investigated. The importance of p-CdTe material is in depositing a good quality absorber layer in solar cells.

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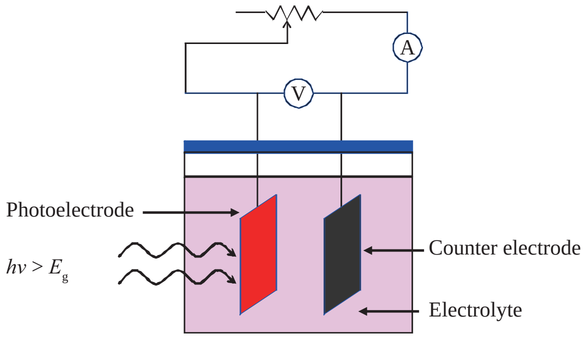


Fig. 1. Experimental circuit diagram for a photoelectrochemical cell formed with a p-CdTe photoelectrode.

2. Experimental

Spray pyrolysis involves the atomization of the precursor solution, spray formation followed by the chemical reaction on a hot substrate. The precursor solution for the spray is prepared by dissolving cadmium chloride ($CdCl_2$) and tellurium dioxide (TeO_2) in a solution containing ammonia and double distilled water in the ratio 1 : 4. During the deposition, to form CdTe on the hot substrate (Glass and fluorine doped tin oxide coated glass substrates), the ionicity of the Te ion should be negative. Hydrazine hydrate ($N_2H_4 \cdot 2H_2O$) is used as a reducing agent to provide the energy necessary to reduce the valency from Te^{4+} to Te^{2+} to create a condition favourable for forming CdTe in the presence of Cd^{2+} ions. The pH of the solution is adjusted using HCl for preparation of a clear, transparent solution. We have deposited the films for various pH values (pH = 10, 10.5, 11), solution quantities (20–40 cc), substrate temperatures (225–300 ℃) and solution concentrations (7.5–15 mM) to obtain good quality photoelectrodes for solar cell application. The resulting films were deposited using compressed air as a carrier gas. Other preparative parameters viz. spray rate = 1.5 cc/min, nozzle to substrate distance = 32 cm, nozzle diameter = 0.05 cm, were kept constant for all experiments. The prepared films were characterized for optimization by using photoelectrochemical, structural, morphological, compositional, thermal and electrical characterization, etc. A schematic experimental circuit diagram for photoelectrochemical (PEC) cell formed with a p-CdTe photoelectrode is shown in Fig. 1. The preparative parameters, such as the pH of solution, quantity, substrate temperature and solution concentration, were optimized by noting the 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 a standard three-electrode configuration, comprising p-CdTe photoelectrodes deposited onto the FTO substrates as an active photoelectrode, graphite as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. A aqueous 1M polysulphide (Na_2S + S + NaOH) was used as the redox electrolyte. These three electrodes were fitted in the bakelite holder, having a thickness of 1 cm and a diameter of 3.5 cm, and fixed in a cylindrical corning glass cell with a capacity of 30 cm^3. The distance between the photoelectrode and the counter electrode was 0.5 cm and the exposed area to illuminating radiation was 1 cm^2. The water lens was interposed between the lamp and the cell to avoid direct heating of the cell. The area of the semiconducting thin film other than that in contact with the electrolyte was covered by epoxy resin (Araldite, India) to avoid any contribution due to base contact of oxide material with the electrolyte and its interference in the measured values of net photocurrent density. The structural characterization of the deposited thin films was carried out by analyzing the X-ray diffraction patterns obtained under Cu-K_α (λ = 1.5406 Å) radiation from a Philips X-ray diffractometer model PW-1710. The surface morphology was studied using a JEOL JSM-6360 scanning electron microscope (SEM), Japan, with an energy dispersive analysis by X-ray (EDAX) analyzer to measure quantitatively the sample composition. The optical spectrum was recorded at room temperature and near to normal incidence using a Jobin-Yvon monochromator, a goniometric setup, a UV-enhanced photodiode (Hamamatsu) and lock-in amplification.

3. Results and discussion

3.1. Photoelectrochemical study

Optimization of preparative parameters for deposition of good-quality and stoichiometric CdTe thin films is essential. Optimization of preparative parameters is carried out by noting the maximum values of I_{sc} and V_{oc} of the PEC cell. Figure 2(a) shows the variation of I_{sc} and V_{oc} with solution pH. From the graph, it is observed that I_{sc} and V_{oc} increase with increasing solution pH, and they attain maximum values for film deposited at 10.5 pH. On further increasing the pH, both I_{sc} and V_{oc} decrease. This indicates the formation of a good-quality and almost stoichiometric compound at 10.5 pH. The lower values of I_{sc} and V_{oc} may be due to an increase in resistivity of the CdTe thin films deviating from stoichiometry. The PEC cell with a configuration of CdTe/0.1 M polysulfide/ graphite is used to check the type of conductivity exhibited by the CdTe thin films. The polarity of the dark voltage is positive toward the CdTe photoelectrode and negative toward the graphite electrode for all samples showing p-type semiconducting behavior. Figure 2(b) shows the variation in I_{sc} and V_{oc} with solution quantity. As the solution quantity increased, the values of I_{sc} and V_{oc} went on increasing up to 30 cc and then decreased for higher quantities. The lower values of I_{sc} and V_{oc} for lower quantities are due to low film thickness, and the maximum values obtained at 30 cc are due to achieving optimum thickness. Variation in I_{sc} and V_{oc} against substrate temperature is shown in Fig. 2(c). The plot shows that I_{sc} and V_{oc} increase with increasing substrate temperature and attain maximum values for the film deposited at 250 ℃, indicating probably a better formation of stoichiometric semiconducting compound. A further increase in substrate temperature decreased the values of I_{sc} and V_{oc}. The lower values of I_{sc} and V_{oc} may be attributed to non-stoichiometric growth of CdTe thin films due to insufficient thermal energy provided during the deposition, while in the case of high temperature, evaporation of solution takes place. Figure 2(d) depicts the plot of I_{sc} and V_{oc} versus solution concentration. The values of I_{sc} and V_{oc} increase with increasing solution concentration up to 10 mM and then decrease for higher solution concentration. Lower values of short circuit current and open circuit voltage for high solution con-

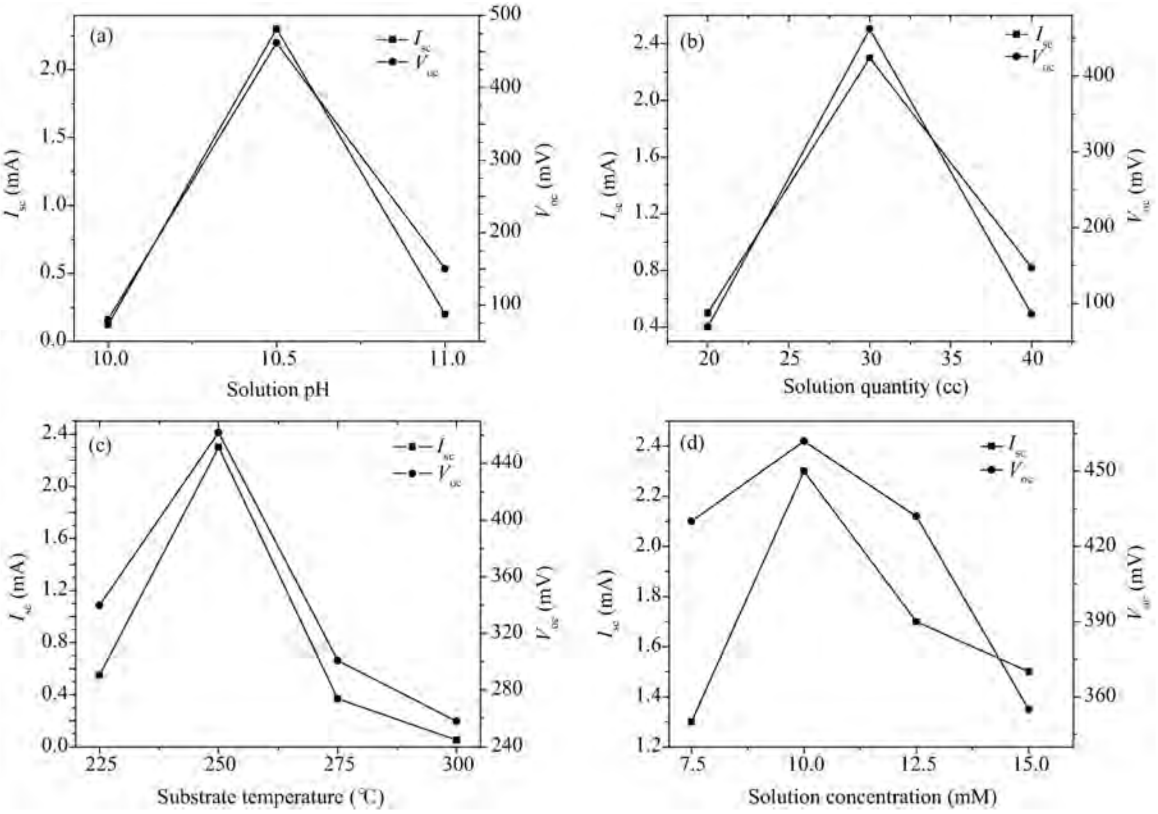


Fig. 2. Variation in I_{sc} and V_{oc} of deposited CdTe thin films with (a) solution pH, (b) solution quantity, (c) substrate temperature, and (d) solution concentration.

centration are due to incomplete growth of compound or partial decomposition and showing the powdery nature of films. From this study, we achieved the good quality photoelectrodes, having optimized parameters such as pH = 10.5, quantity = 30 cc, substrate temperature = 250 ℃ and solution concentration = 10 mM, showing maximum short circuit current (I_{sc} = 2.3 mA) and open circuit voltage (V_{oc} = 462 mV).

In the dark and under illumination, the current–voltage (I–V) characteristics of glass/fluorine doped tin oxide/cadmium telluride/SCE cells were measured. The efficiency (η%) and fill factor (FF) are calculated from the relations

$$\eta(\%) = \frac{V_{oc} I_{sc} \mathrm{FF}}{P_{input}} \times 100, \tag{1}$$

$$\mathrm{FF} = \frac{I_{max} V_{max}}{I_{sc} V_{oc}}, \tag{2}$$

where P_{input} is the input light intensity, and I_{max} and V_{max} are the values of maximum current and maximum voltage, respectively, that can be extracted from a PEC solar cell. From I–V measurements, it was observed that the higher magnitude of I_{sc} = 2.3 mA, V_{oc} = 462 mV, FF = 0.48 and η = 3.4% are obtained for the films deposited at 250 ℃ and 10 mM solution concentration using polysulphide as an electrolyte. The compact and densely packed CdTe crystallites can absorb enough light. Furthermore, the photogenerated electrons can transport directly through cubic crystallites and compact layers to the conducting substrates with minimum loss. This greatly reduces the recombination losses of photogenerated charge carriers due to a decrement in grain boundary resistance in the charge transportation process.

3.2. Structural analysis

Figures 3(a) and 3(b) shows the X-ray diffraction patterns of deposited films at different substrate temperatures and precursor solution concentrations. Comparison of standard and observed d values of CdTe thin films deposited at various temperatures and solution concentrations is shown in Tables 1 and 2. The data are analyzed by making use of Joint Committee for Powder Diffraction Standards (JCPDS) card No. 15-770. The films are polycrystalline and fit well with the cubic crystal structure with preferred orientation along the (111) plane. The reason for relatively lower peak intensities is the lower film thickness and formation of a nanocrystalline phase in the films. Some weak reflection, such as (200), (220), (311), (222) and (400), have also been observed but with small intensities. The intensity of strong orientation along the (111) plane increases with substrate temperature up to 250 ℃ and then decreases for higher temperatures. The diffraction angle of the (111) peak is almost in agreement with the CdTe bulk single crystal[14], implying that no evident residual stress or inclusion-induced lattice distortion has been developed in the film due to temperature. When the solution concentration increases, the intensity of the (111) peak increases up to a 10 mM concentration and then decreases for higher concentrations. As the solution concentration increases, the crystallinity of the films increases, maybe due to the sufficient increase in growth of the grains. Further increase in solution concentration peak intensity de-

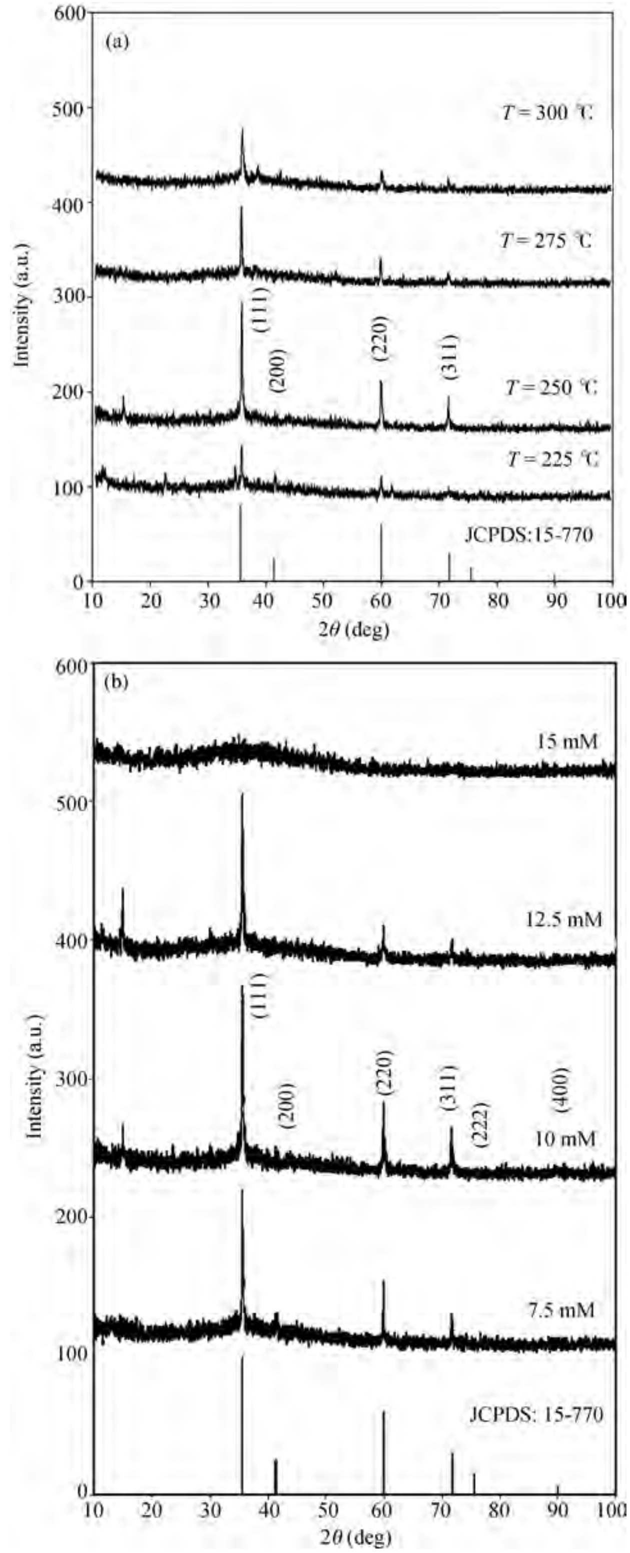


Fig. 3. X-ray diffraction patterns of CdTe thin films deposited at various (a) substrate temperatures and (b) solution concentrations.

Table 1. Comparison of observed and standard d values for the CdTe thin films deposited at various substrate temperatures.

Standard d value (Å)	Observed d value (Å) 225 ℃	250 ℃	275 ℃	300 ℃	Reflection
3.742	3.7415	3.7425	3.7441	3.7410	(111)
3.270	3.2269	–	–	–	(200)
2.290	2.2904	2.2913	2.2951	2.2872	(220)
1.954	1.9538	1.9557	1.9561	1.9554	(311)

Table 2. Comparison of observed and standard d values for the CdTe thin films deposited at various solution concentrations.

Standard d value (Å)	Observed d value (Å) 7.5 mM	10 mM	12.5 mM	15 mM	Reflection
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. Variation in crystallite size with respect to substrate temperature and solution concentration.

Substrate temperature (℃)	Crystallite size (nm)	Solution concentration (mM)	Crystallite size (nm)
225	32	7.5	22
250	27	10	27
275	35	12.5	23
300	41	15	19

creases is attributed to the non-uniform and rough powdery films. The observed full width at half maximum (FWHM) is corrected using single crystal Si peak broadening.

The crystallite size D is calculated using Scherrer's formula[15],

$$D = \frac{0.9\lambda}{\beta\cos\theta}, \tag{3}$$

where D is the crystallite size, β is the broadening of the diffraction line measured at half of its maximum intensity (rad) FWHM, λ is the X-ray wavelength (1.5406 Å), and θ is Bragg's diffraction angle. From Table 3, it is seen that as the solution concentration increases, the average crystallite size increases up to 10 mM concentration and tends to decrease afterwards. The tendency of a decrease in crystallite size with an increase in concentration after 10 mM may be due to super-saturation of atoms. Also, the crystallite size decreases with substrate temperature, attaining the lowest value of 27 nm at 250 ℃ and then increasing for higher temperatures.

The strain generated in deposited films is calculated by using the formula[16]

$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon\tan\theta, \tag{4}$$

where ε is the strain. The dislocation density is defined as the length of dislocation lines per unit volume of the crystal[17]. The dislocation density is calculated using the formula[18]

$$\delta = \frac{1}{D^2}, \tag{5}$$

where δ is the dislocation density. Figures 4(a) and 4(b) show the variation of dislocation density (δ) and strain (ε) generated in films with substrate temperature and solution concentration, respectively. The dislocation density and strain increase with respect to the substrate temperature up 250 ℃ and then they decrease. As the solution concentration increases, the dislocation

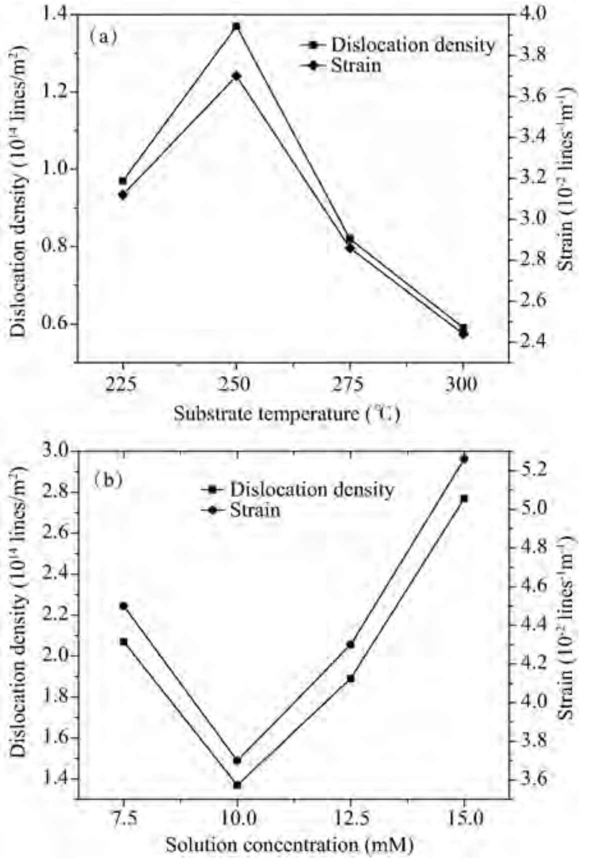


Fig. 4. Variation in dislocation density and strain with respect to (a) substrate temperature and (b) solution concentration of CdTe thin films.

density and strain generated in the films decrease with solution concentration and films prepared at 10 mM are found to have a minimum value of dislocation density and strain. Thereafter, the dislocation density and strain increase. Due to the release defects in the lattice, the strain in the films gets released and a minimum value of strain is obtained for films prepared at 10 mM. CdTe thin films with lower strain and dislocation density improve the stoichiometry of the films, which in turn causes volumetric expansion of the films. The variation in crystallite size, strain and dislocation density with respect to the solution concentration indicates that the strain and dislocation density decrease whereas the crystallite size increases.

The texture coefficient (TC) represents the texture of a particular plane, whose deviation from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation is obtained from different TCs (hkl) defined by the well-known relation[19]

$$\mathrm{TC}(hkl) = \frac{\dfrac{I(hkl)}{I_0(hkl)}}{\dfrac{1}{N}\sum_N \dfrac{I(hkl)}{I_0(hkl)}}, \qquad (6)$$

where $I(hkl)$ is the measured intensity, $I_0(hkl)$ is the JCPDS intensity and N is the reflection number. Figure 5 depicts the variation in the texture coefficient with substrate temperature for the (111) plane. TCs of the (111) plane for the films deposited initially increases up to 250 ℃ and decreases later. The observed TC along the (111) plane is about 1.7 at the optimized substrate temperature due to enhancement in the crystallinity and stoichiometric films.

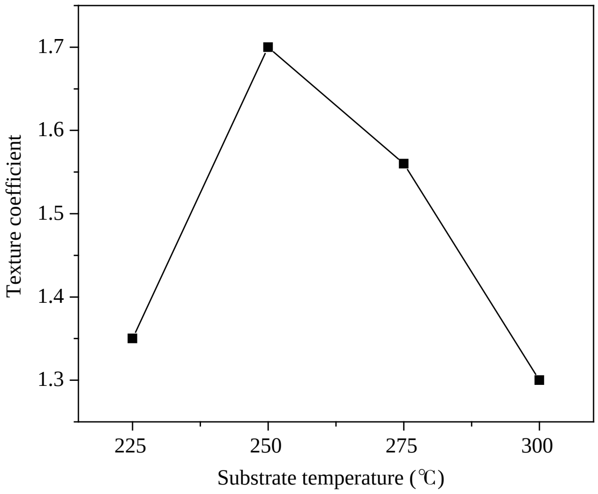
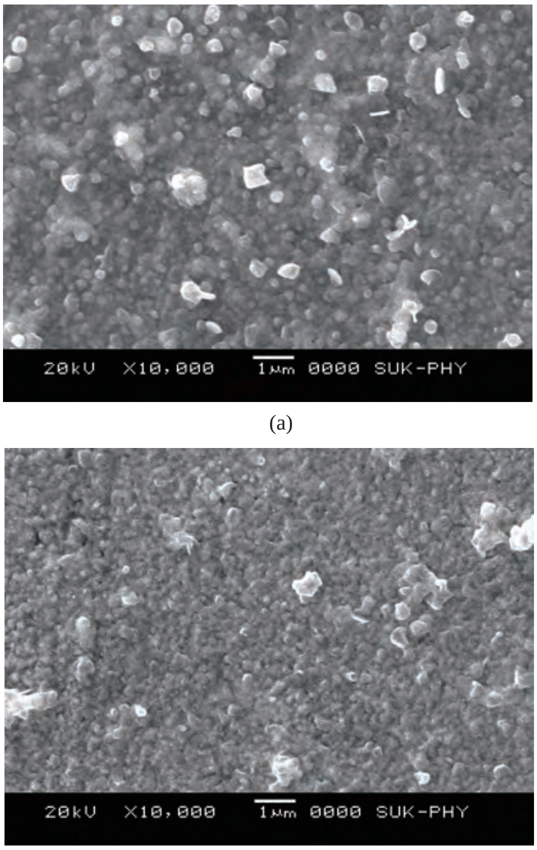


Fig. 5. Variation in texture coefficient along the (111) plane with respect to substrate temperature of CdTe thin films.



(a)

(b)

Fig. 6. Scanning electron micrographs of CdTe thin films deposited at (a) optimized substrate temperature (250 ℃) and (b) optimized solution concentration (10 mM).

3.3. Morphological study

Figure 6 shows micrographs of CdTe thin films deposited at the optimized substrate temperature (250 ℃) and solution

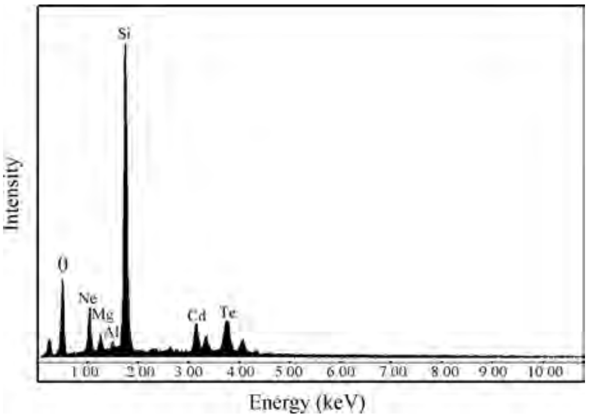


Fig. 7. EDAX spectrum of CdTe thin films deposited for optimized solution concentration (10 mM) at 10.5 pH, 30 cc quantity and 250 ℃ temperature.

concentration (10 mM). The micrograph shows that the substrate is well covered with a large number of densely packed well oriented cubic polycrystalline grains. The SEM pictures show the as-deposited CdTe to be of large grain size, uniform coverage and low porosity. At the optimized concentration, well covered, uniform, rounded, densely packed grains on the surface are observed. The average size of the grains is found to be 70–150 nm. The film composition has been analyzed using energy dispersive analysis by X-rays set up attached to a scanning electron microscope. The compositional analysis of the CdTe thin film deposited at optimized preparative parameters is carried out by the EDAX technique shown in Fig. 7. The EDAX study shows that the Cd–Te ratio is almost stoichiometric.

3.4. Optical absorption study

The optical absorption of the films has been studied in the range 380–950 nm. The variation in optical density with wavelength is analyzed to find out the nature of the transition involved and the optical band gap. The nature of the transition is determined by using the relation

$$\alpha = \frac{A(h\nu - E_{\mathrm{g}})^n}{h\nu}, \tag{7}$$

where α is the absorption coefficient, E_{g} is the band gap of material, 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 8 shows variation in $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ for CdTe thin films deposited at optimized preparative parameters. The plot exhibits almost linear variation towards the lower wavelength side and follows exponential behavior as the 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 $\alpha = 0$ is 1.5 eV. The results are in good agreement with those reported by others[20].

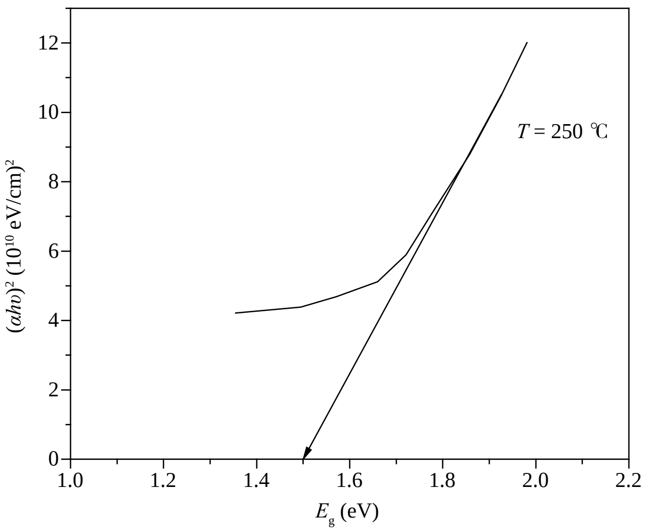


Fig. 8. Direct band gap spectrum of CdTe thin films deposited for optimized solution concentration (10 mM) at 10.5 pH, 30 cc quantity and 250 ℃ temperature.

4. Conclusions

The synthesis and characterization of p-CdTe thin films deposited by spray pyrolysis under different preparative conditions have been investigated. The results clearly show the role of different preparative parameters viz solution pH, solution quantity, substrate temperature and solution concentration on the deposited films in order to get good-quality photosensitive material. Structural analysis shows that the films are polycrystalline with a cubic crystal structure. The crystallinity and texture coefficient increase up to the optimized substrate temperature and solution concentration and then decrease later. The dislocation density and strain show a reverse nature to temperature and concentration. Micrographs show that the film surface is well covered by uniformly distributed grains with varying sizes. The stoichiometry of the deposited films is confirmed by using EDAX analysis. The observed direct band gap for optimized parameters is about 1.5 eV. Finally, it is concluded that the CdTe thin films are potential candidates for solar cell applications.

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