Effect of Post Deposition Heat Treatment on Microstructure Parameters, Optical Constants and Composition of Thermally Evaporated CdTe Thin Films

P.K.K. Kumarasinghe^a, Amila Dissanayake^b, B.M.K. Pemasiri^{a,c} and B.S. Dassanayake^{a,c,*}

^aPostgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

^bDepartment of Physics and Astronomy, Western Michigan University, Kalamazoo, MI 49008, USA

^cDepartment of Physics, University of Peradeniya, Peradeniya, Sri Lanka

Abstract

Thin film microstructure and its properties can be effectively altered with post deposition heat treatments. In this respect, CdTe thin films were deposited on glass substrates at a substrate temperature of 200 °C using thermal evaporation technique, followed by air annealing at different temperatures from 200 to 500 °C. Structural analysis reveals that CdTe thin films have a cubic zincblend structure with two oxide phases related to CdTe₂O₅ and CdTeO₃ at annealing temperature of 400 and 500 °C respectively. Regardless of the annealing temperature, the plane (111) was found to be the preferred orientation for all films. The crystallite size was observed to increase with annealing temperature. All films were found to display higher lattice parameters than the standard, and hence found to carry a compressive stress. Optical measurements suggest high uniformity of films both before and after post deposition heat treatment. Films annealed at 400 °C displayed superior optical properties due to its high refractive index, optical conductivity, relative density and low disorder. Furthermore, according to the compositional measurements, CdTe thin films were found to exhibit Te rich and Cd rich nature at regions near the substrate and center of the film respectively, for all annealing temperatures. However, composition of the regions near the substrate was found to become more Te rich with increasing annealing temperature. The study suggests that changing the annealing temperature as a post deposition treatment affects structural and optical properties of CdTe thin film as well as its composition. According to the observations, films annealed at 400 °C can be concluded to be the best films for photovoltaic applications due to its superior optical and structural properties.

Keywords: CdTe, thermal evaporation, annealing temperature, structural, optical, compositional

* Corresponding author: E-mail: buddhikad@pdn.ac.lk, buddhid@gmail.com
(B.S. Dassanayake)

1. Introduction

Cadmium telluride (CdTe) is an important II–VI semiconducting material which exists in either zincblende (cubic) or wurtzite (hexagonal) structure with an ideal direct band gap of 1.45 eV at room temperature and an absorption coefficient greater than $1 \times 10^5 \text{ cm}^{-1}$ near the absorption edge, suited for effective photovoltaic energy conversion [1,2]. CdTe can exhibit both n-type and p-type conductivity, which makes it useful for both homo junction and hetero junction configurations. Fabrication of optoelectronic devices, photovoltaic cells, laser windows, gamma ray detectors and p-n diodes are some of its potential applications because of its optimum band gap as well as its high absorption coefficient [3].

Various techniques have been employed to deposit CdTe films, such as, closed space sublimation [4], electron beam evaporation [5], RF magneto sputtering [6], hot wall epitaxy [7], pulsed laser deposition [8], pulsed laser evaporation [9], molecular beam epitaxy [10], chemical vapor deposition [11], electrodeposition [12] and thermal evaporation [13]. Out of these methods, thermal evaporation stands out due to its low level of impurity presence in the growing layer, low trend of oxide formation, straight-line propagation of vapors from source to substrate, high deposition rate, low material consumption as well as low cost of operation. Therefore, thermal evaporation is considered as an attractive method of fabricating high quality thin films [14].

Currently, the modification of various properties of CdTe films by altering both deposition conditions as well as post-deposition treatments is a matter of much research work. Many of the properties of CdTe thin films such as structural, optical, morphological, electrical and compositional are strongly dependent upon the fabrication techniques, film thickness, substrate, CdCl_2 treatment, doping and substrate temperature [15]. Among them, the post-deposition heat treatment is one of the most effective and simplest ways to tune the above mentioned properties of CdTe films [3].

Recrystallization treatments are widely used for the CdTe thin films as they are essentially required for high efficiency device fabrication. One of the simplest methods of initiating recrystallization is through post deposition heat treatment of deposited films. When heat treated, optical, structural, electrical, compositional as well as morphological properties can be effectively improved [16-18].

In this work, the influence of annealing temperature on optical properties has been studied using UV-visible spectroscopy, structural properties via grazing incidence X-ray diffraction (GIXRD) technique and depth profiling using energy dispersive X-ray (EDX) spectroscopy. Additionally, scanning electron microscopy (SEM) was employed for morphological characterizations.

2. Experimental details

CdTe thermal evaporation was done using an alumina crucible with commercially available CdTe powder (Sigma-Aldrich, < 250 μm , deposition grade, $\geq 99.99\%$). The chamber was at a pressure better than 2×10^{-5} Torr by combination of rotary and diffusion pumps. Thin films of CdTe were deposited on clean soda lime glass substrates using Edwards Vacuum Coating Unit, by maintaining the thickness at $5 \mu\text{m}$ using SQM-160 Multi-Film Rate/Thickness Monitor, keeping substrates fixed at 12 cm above the crucible. The temperature of the crucible was kept constant at 650°C . Prior to deposition of CdTe films on soda lime glass substrates, the substrates were cleaned using the standard cleaning procedure [19,20]. During the process of deposition, the substrate temperature was maintained constant at 200°C using a resistance heating system. Deposited CdTe thin films were later air-annealed at 200, 300, 400 and 500°C for 20 min.

Structural properties of the thin films were analyzed employing Philips X'Pert X-ray diffractometer GIXRD using $\text{CuK}\alpha$ radiation with $\lambda = 1.54184 \text{ \AA}$ in continuous mode at generator voltage of 45 kV in 40 mA tube current using 0.02° scan step size with the step time of 5 s and 2θ in the range of $10^\circ - 100^\circ$. Optical measurements of deposited films were conducted using UV-1800 Shimadzu Double Beam UV/VIS Spectrometer. Atomic compositions of CdTe thin films were analyzed by micro analytical technique of EDX spectroscopy using INCA X-act SN 67217 EDX under accelerating voltages of 10 keV. Morphological analysis was conducted using ZEISS EVO|LS15 SEM under a beam current of $30 \mu\text{A}$.

3. Results and discussion

3.1. Structural analysis

Film structures formed during fabrication and after recrystallization process as a result of post deposition treatments strongly affect the properties of thin films. Hence, detailed structural analysis is of utmost importance to understand the behavior of the semiconductor film, especially in high quality device fabrication processes. Therefore, structural variation of deposited CdTe thin films with respect to annealing temperature was studied using GIXRD measurements.

Fig. 1 shows diffractograms of CdTe thin films treated at different annealing temperatures from 200 to 500 °C after annealing for 20 min, along with an as-deposited film. All films were deposited at a substrate temperature of 200 °C. When annealed, the films were found to possess a polycrystalline nature with cubic zincblende structure for films annealed above 300 °C, as a result of recrystallization. Reflections corresponding to (111), (220), (311), (400), (331), (422), (511), (440), (531) and (620) plane orientations according to ICDD-PDF file 00-015-0770 were identified for films annealed at higher temperatures as seen in Fig. 1(a) to (c). No phase change of CdTe thin films was observed with varying annealing temperature. However, few additional diffraction peaks were found to emerge with increasing annealing temperature.

Fig. 2 shows the enlarged GIXRD pattern from 10° to 35°. The additional weak diffraction peaks at 10.34 ° and 20.82 ° corresponding to CdTe₂O₅ for films annealed at 400 °C and peaks at 29.45° and 32.39° along with a strong peak at 12.27° corresponding to CdTeO₃ for films annealed at 500 °C were identified from ICDD-PDF file 43-0343 and 77-1906 respectively. No oxide phases were observed for films annealed below 400 °C.

The as-deposited CdTe thin film, which was fabricated at a substrate temperature of 200 °C exhibits a strong (111) preferred orientation as seen in Fig. 1(e). Thereafter, the intensity of the (111) diffraction peak gradually decreases with increasing annealing temperature until it reaches 300 °C. Quantitative information regarding such preferential orientations of crystallites along a crystal plane (*hkl*) can be described by the texture coefficient (C_{hkl}) [21,22].

$$C_{hkl} = \frac{\frac{I_{(hkl)}}{I_{0(hkl)}}}{\frac{1}{N} \sum^N \frac{I_{(hkl)}}{I_{0(hkl)}}} \quad (1)$$

Here, $I_{(hkl)}$ is the measured intensity, $I_{0(hkl)}$ is the intensity of the standard sample (ICDD-PDF file 00-015-0770) and N is the number of reflections. The C_{hkl} gives a measure of the enhancement of the (hkl) reflection in comparison to a completely randomly oriented sample. Fig. 3 shows the variation of C_{111} (C_{hkl} of (111) plane) with respect to annealing temperature.

Irrespective of the annealing temperature, (111) plane was found to be the preferred orientation for all annealed films. As seen in Fig. 3 and Table 1, the C_{111} for films annealed at 200 °C was the highest compared to the rest, while it was found to slightly increase with increasing annealing temperature beyond 300 °C.

The degree of orientation (σ) of the films can be calculated by the standard deviation of all C_i values, using the equation [1,23];

$$\sigma = \sqrt{\sum_{i=1}^n \frac{1}{n} (C_i - C_{io})^2} \quad (2)$$

where, C_i is the texture coefficient of the plane i , C_{io} is the texture coefficient of the standard sample and n is the number of planes considered. Value of zero for σ indicates that the sample is completely at random orientation while larger values suggest better orientation. Calculated values of σ are shown in Fig. 4 and Table 1. According to the figure, film annealed at 200 °C is better oriented compared to the rest, while lowest orientation was found at 300 °C. Furthermore, degree of orientation was found to increase with increasing annealing temperature beyond 300 °C.

It was also observed that all the diffraction peaks in Fig. 1 were slightly shifted towards the lower side when compared to standard sample (ICDD-PDF file 00-015-0770), suggesting potential deviations of the corresponding lattice parameter (a_0) of the film. Hence, a_0 values were calculated for all the films annealed at different temperatures to study the effect of annealing

temperature on a_0 . Lattice parameter related to each peak of the GIXRD pattern was determined using the relation,

$$a_o = d\sqrt{h^2 + k^2 + l^2} \quad (3)$$

where, $d = \lambda/2\sin\theta$ and h, k, l are the Miller indices for the diffraction peaks. The Nelson and Taylor method [23,24] was used to calculate a_0 values. In this method the values of a_0 calculated for different peaks were plotted against $\cos^2\theta((\sin\theta)^{-1} + \theta^{-1})$, and the lattice parameter of the thin film was obtained by the intercept of the graph. The variation of calculated a_0 with respect to annealing temperature is shown in Fig. 5 and Table 1. According to the results, lowest a_0 value was determined to be within the annealing temperature range of 300 to 400 °C. Furthermore, it can be inferred that all the annealed films are under compressive stress, since the calculated a_0 values are greater than that of the standard powder sample (6.481 Å).

Stress developed in a thin film is twofold; intrinsic and extrinsic. Intrinsic stress can be caused by the conditions prevailing during the deposition of the film (substrate temperature, deposition rate etc.), whereas extrinsic stress can be caused by the difference in the thermal expansion coefficients between substrate and thin film [25]. It is evident from Fig. 1(d) that the films annealed at 200 °C display low crystallinity compared to the other annealed films. This suggests the existence of high intrinsic defects and hence high intrinsic stress, resulting in high a_0 values. On the other hand, higher a_0 value seen at 500 °C can potentially be due to extrinsic stress caused by thermal mismatch.

The variation of crystallite size with respect to annealing temperature can be studied using Williamson Hall (WH) plots [23,26] via;

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4\varepsilon \sin\theta \quad (4)$$

where, K is the shape factor, λ is the wave length of X-rays used for the measurement, D is the crystallite size, ε is the micro strain, β_{hkl} is the full width at half maximum (FWHM) of the diffraction peak at 2θ and θ is the diffraction angle. The crystallite size was calculated from the

intercept of the linear plot between $\beta_{hkl} \cos \theta$ and $\sin \theta$. Both $\beta_{hkl} \cos \theta$ and $\sin \theta$ values were calculated for each diffraction peak in a particular diffraction pattern of a fabricated thin film. Calculated crystallite sizes are shown in Fig. 6. According to the figure, the crystallite size was found to increase with increasing annealing temperature. Calculated crystallite size values are summarized in Table 1.

At higher annealing temperatures, the atomic, ionic, or molecular species of CdTe formed on the substrate surface acquire a large thermal energy and hence a large mobility. Therefore, a large number of nuclei are formed which coalesce to form a continuous film with large grains on the substrate at higher temperature, producing larger crystallites [3]. Hence, crystallite sizes are expected to increase with annealing temperature. Furthermore, second and third line of the First paragraph after equation 4 were changed as

Crystalline imperfections can degrade both the optical and electrical properties of a device [27]. It is well known that growth mechanism and post deposition treatments are highly influential on the defect density of thin films. Dislocation density (δ) of a film provides information regarding imperfections of a crystal lattice. Therefore, dislocation density was calculated using Williamson and Smallman's relation [28,29];

$$\delta = \frac{1}{D^2} \quad (5)$$

Calculated values are shown in Fig. 7 and Table 1. According to the figure, dislocation density was found to reduce with increasing annealing temperature.

The lattice strain which is developed as a result of displacement of the atoms with respect to their reference lattice positions is known as micro strain (ε) [15]. This disarrangement of lattice is created during fabrication process of a thin film [30]. Micro strain (ε) of the films was calculated to study the influence of annealing temperature using the WH plots, from the gradient of the equation (4). The calculated values for the micro strain are shown in Fig. 8 and Table 1. The lowest micro strain was found for films annealed at a temperature of 300 °C.

The stress of the preferred orientation (111) was calculated to study the dependency of stress on annealing temperature. For stress fields in thin films that follow the biaxial stress

model, a single in-plane stress component σ_ψ is sufficient to account for the full stress tensor [31]. Clemens and Bain have developed a formula to calculate σ_ψ for films textured along the (111) orientations, typical for FCC materials. Using this relationship, σ_ψ can be calculated by estimating the magnitude of strain (ε_ψ) as shown below [32-34].

$$\varepsilon_\psi = \frac{d_\psi - d_0}{d_0} \quad (6)$$

$$\varepsilon_\psi = \sigma_\psi \left(\frac{2S_{11} + 4S_{12} - S_{44}}{3} + \frac{S_{44}}{2} \sin^2 \psi \right) \quad (7)$$

where, ε_ψ is the strain at an angle ψ from the surface normal of thin film, d_ψ and d_0 are the interplanar distances for CdTe thin film and powder sample respectively. Here, S_{11} , S_{12} and S_{44} are the components of the 6×6 compliance array for CdTe. The values of S_{11} , S_{12} and S_{44} for CdTe are 4.27×10^{-12} , -1.73×10^{-12} and 5×10^{-12} cm²/dyn respectively [35]. The calculated values of in-plane stresses of (111) plane are presented in Table 2. It can be observed from the table that, the stress decreases with increasing annealing temperature up to 500 °C. As-deposited films yield a maximum value of -556.7 MPa, while the minimum value of -284.0 MPa was observed for the films annealed at a temperature of 500 °C.

The stress of a film can directly influence its optical band gap. Hence the optical band gap variation due to the influence of stress of (111) plane was calculated. The influence of the stress parallel to the (111) direction of zinc-blende CdTe structure on band gap (E_g), for first-order approximation can be written as [25];

$$E_g^{(111)}(\sigma_\psi) = E_g(0) + \delta E_H - \frac{1}{2} \delta E_{(111)} \quad (8)$$

$$\delta E_H = \alpha (S_{11} + 2S_{12}) \sigma_\psi \quad (9)$$

$$\delta E_{(111)} = \frac{\gamma S_{44} \sigma_\psi}{3^{1/2}} \quad (10)$$

where, $E_g(0)$ is the stress free value of the band gap (1.529 eV) [36], α and γ are the deformation potentials for CdTe, with $\alpha = -3.4$ eV and $\gamma = -4.8$ eV [25]. The estimated value of the change in the band gap due to stress in the CdTe films was calculated from the above equations was found

to be in the range between -12 and -23 meV (the negative sign indicates a value lower than $E_g(0)$).

3.2. Morphological analysis

Since restructuring due to annealing can directly affect the morphology, SEM images of the surfaces were obtained for all the investigated films. According to the results shown in Fig. 9, the films annealed below 400 °C are free of voids and possess no significant change in morphology with better uniformity compared to films annealed at 500 °C, where large grain size with highly non-uniform surfaces are observed. However, films annealed at 400 °C show densely packed nature with a void free uniform surface, suggesting a better quality film compared to the rest.

3.3. Optical analysis

Recrystallization of CdTe thin films strongly depends on the annealing temperature, altering many properties like crystallite size, intrinsic defects and stress, slightly shifting the optical absorption edge. Accordingly, it is important to understand the behavior of optical properties with annealing temperature as it is one of the most important tools of determining the band structure of semiconductors.

Fig. 10 shows the transmittance spectra in the wavelength range from 400 to 1100 nm for CdTe thin films annealed at different temperatures. The transmittance in the visible region is found to be nearly zero before a steep increase around 825 nm. All the transmittance spectra reveal interference effects for wavelengths beyond the absorption edge. Such behavior of the transmittance spectra is an evidence of the thickness uniformity of the fabricated thin films [3,37]. However, the interference pattern is less pronounced for the films annealed at 500 °C, revealing non-uniform nature of the film, which can be justified by the SEM image of the film in Fig. 9(e).

The absorption coefficient (α) of CdTe thin films was calculated from the optical transmittance measurements using;

$$\alpha = \frac{2.303}{d} \log \left[\frac{1}{T} \right] \quad (11)$$

where, T is the transmittance and d is the thickness of the film. The absorption coefficient can be written in general form as a function of incident photon energy as;

$$\alpha h\nu = A(h\nu - E_g)^n \quad (12)$$

where, A is a constant, h is the Planck's constant, ν is frequency of the incident radiation, E_g is the optical band gap. The value of n depends upon the nature of transition. For the direct and allowed cases $n = 1/2$, for the direct but forbidden cases $n = 3/2$, but for the indirect and allowed case $n = 2$ and for the indirect and forbidden cases it is 3 or more. By analyzing the trend of α with respect to photon energy, it was determined that the fabricated CdTe thin films have a direct band gap behavior and hence, n can be considered as $1/2$ and the extrapolation of the linear region of $(\alpha h\nu)^2$ vs. $h\nu$ plot at $\alpha = 0$, as seen in the Fig. 11, gives the direct energy band gap value [38-42]. The E_g values which were calculated accordingly for CdTe thin films annealed at different annealing temperatures are shown in Fig. 12 and Table 3.

The deviation of E_g can be due to the effects such as variation of particle size, stress and intrinsic defect density etc. At lower annealing temperatures, there can be two opposing effects on the energy of the absorption edge; (1) effect of growing which lead to a shift of absorption to lower energy side and (2) the reduction of intrinsic defects which causes a slight shift of absorption to higher energy side. The combination of these two effects leads to a small shift in energy of the absorption edge [43]. Therefore the shift in E_g to the lower energy side with increasing annealing temperature can be concluded to be due to combination of increment of particle size, decrease in intrinsic defects as well as stress.

With the aid of the interference fringes seen in Fig. 13, it is possible to calculate the optical constants of the deposited CdTe film. The interference free transmittance (T_a) can be calculated using the formula [44];

$$T_\alpha = \sqrt{T_M T_m} \quad (13)$$

T_M and T_m are the transmittance maximum and the corresponding minimum at a certain wavelength as seen in Fig. 13.

Complex refractive index can be written as $n_c = n + ik$ where, n and k are refractive index and extinction coefficient respectively [45]. Refractive index is one of the fundamental properties of materials as it is closely related to the electronic polarizability of ions, local field inside the material as well as the transmittance [3]. The value of n was calculated by using Swanepoel method which is based on Manifacier *et al.* [46]. In this method, interference free transmittance is evaluated using extrema in transmittance spectra to calculate n using the relation [44];

$$n = \left[H + (H^2 - s^2)^{1/2} \right]^{1/2} \quad (14)$$

$$H = \frac{4s^2}{(s^2 + 1)T_\alpha^2} - \frac{s^2 + 1}{2} \quad (15)$$

where, H is the Swanepoel coefficient and s is the refractive index of the substrate. The dispersion of n with respect to wavelength for films fabricated at different annealing temperatures is shown in Fig. 14. Calculated n values at 1050 nm are summarized in Table 3. According to the figure, anomalous dispersion of the refractive index can be observed near the absorption edge (characteristic frequency of the electron). Anomalous dispersion is attributed to the equality between the frequency of electromagnetic radiation and the plasma frequency that makes the electrons in CdTe thin film to couple with oscillating electric field [47]. Furthermore, n becomes larger when the frequency of the radiation is greater than the absorption edge. When the frequency decrease below the absorption edge, one can see that n gradually decreases. According to Fig. 14, the highest refractive index was found for the films annealed at a

temperature of 400 °C. The physical interpretation of the variation of n can be ascribed due to the variation of both density as well as electronic structure of the material [48]. Even though the crystallinity of the films were found to improve with annealing temperature according to the Fig. 6, the emerging of strong oxide peaks at 500 °C, as seen in Fig. 2(a), can cause deterioration of CdTe crystallinity. Therefore, films annealed at 400 °C can be identified as films with best crystallinity. This can be a reason for the recorded higher refractive index of CdTe at 400 °C [37, 23].

In order to calculate the other relevant optical constants, absorbance (x) was estimated using equation (16) which was derived from the method proposed by Connell and Lewis [44,49];

$$x = \frac{P + [P^2 + 2QT_\alpha(1 - R_2R_3)]^{1/2}}{Q} \quad (16)$$

where,

$$Q = 2T_\alpha(R_1R_2 + R_1R_3 - 2R_1R_2R_3) \quad (17)$$

$$P = (R_1 - 1)(R_2 - 1)(R_3 - 1) \quad (18)$$

$$R_1 = [(1 - n)/(1 + n)]^2 \quad (19)$$

$$R_2 = [(n - s)/(n + s)]^2 \quad (20)$$

$$R_3 = [(s - 1)/(s + 1)]^2 \quad (21)$$

Using the calculated x , the absorption coefficient (α) was determined by the formula [44];

$$x = \exp(-\alpha d) \quad (22)$$

where, d is the thickness of the film. The calculated values are plotted in the Fig. 15. Since n becomes larger when the frequency of the radiation is greater than the absorption edge, there is no propagation of radiation through CdTe film attributing to high absorption coefficient in this region. According to the result, α rapidly decreases at the absorption edge with increasing

wavelength. In the weak absorption region, α gradually decrease with increasing wavelength for all films. The α value of CdTe films at 1050 nm is summarized in Table 3. It is seen that α is found to increase with increasing annealing temperature and maximized for films annealed at 400 °C.

The extinction coefficient (k) provides information about the absorption of light in the medium of the material due to inelastic scattering [44]. Extinction coefficient was calculated using the formula [50];

$$k = \frac{\alpha\lambda}{4\pi} \quad (23)$$

where, λ is the wavelength. Variation of k with respect to wavelength is shown in Fig. 16. According to the figure, k was found to decrease with increasing wavelength. Furthermore, k values calculated at 1050 nm, as seen in Table 3, illustrates highest extinction coefficient for films annealed at 400 °C.

The dielectric constant of a material is closely related to the electronic structure of the material and directly relates with the density of states within the forbidden gap and affects the electromagnetic radiations moving through the material [3]. Complex dielectric constant can be written as $\varepsilon = \varepsilon_1 + i\varepsilon_2$; where, ε_1 and ε_2 are real and imaginary parts of the complex dielectric constant respectively. Dielectric constant was calculated using the formula [51];

$$\varepsilon_1 = n^2 - k^2 \quad (24)$$

$$\varepsilon_2 = 2nk \quad (25)$$

Variations of ε_1 and ε_2 with respect to the wavelength are shown in Fig. 17 and 18 respectively. Anomalous dispersion of dielectric constant was observed near the absorption edge, before leveling off at high wavelength values. According to the figure it is clear that high

dielectric constants are observed at 1050 nm, for the films annealed at 400 °C as indicated in both Fig. 17, 18 and Table 3.

Relative density of CdTe thin films can be estimated using Lorentz–Lorentz relation [3];

$$\rho = \left(\frac{n_f^2 - 1}{n_f^2 + 1} \right) \left(\frac{n_b^2 + 1}{n_b^2 - 1} \right) \quad (26)$$

where, n_f and n_b are refractive indices of fabricated thin film and bulk of CdTe respectively. Calculated values at 1050 nm are shown in Fig. 19 and Table 3. According to the figure, highest relative density was observed for film annealed at a temperature of 400 °C. Relative density of films can increase as a result of the reduction of number of grain boundaries and defects with increasing annealing temperature. According to Fig. 1, 6 and 7, crystallinity of the films annealed at 400 °C was found to be superior compared to the rest, justifying the high relative density values obtained. However, CdTe film can be deteriorated at high annealing temperature due to re-evaporation of material from the surface and oxide formation etc., attributing to a decrease in relative density for films annealed at 500 °C.

The optical conductivity (σ_o) is one of the powerful tools for studying the electronic states in materials and can be calculated using the formula [52-54];

$$\sigma_o = \frac{\alpha mc}{4\pi} \quad (27)$$

where, c is the speed of light. According to the Fig. 20, the optical conductivity increases with decreasing wavelength. Rapid increment of σ_o was observed with reducing wavelength beyond absorption edge. This is due to high absorption of incident radiation with excitation of electrons by the high photon energy. The highest optical conductivity was observed for the film annealed at 400 °C in the weak absorption region as seen in Table 3.

Urbach tail in optical absorption near band edge can be observed in materials having disorder of different origins. These disorders create localized states producing an absorption tail,

extending deep into forbidden gap. This absorption tail is known as Urbach tail and the energy associated with this tail is referred to as Urbach energy. Accordingly, this Urbach energy can be determined by the relationship between α and $h\nu$ near the optical band edge and is known as Urbach empirical rule [47,55-58];

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_U}\right) \quad (28)$$

where, α_o is a constant, $h\nu$ is incident photon energy and E_U (Urbach energy) is width of the band tail of localized states in the band gap. The graph of $\ln(\alpha)$ vs. $h\nu$ has a linear behavior near the absorption edge. Accordingly, E_U can be determined using the gradient of the linear fit near the absorption edge. Calculated values using this method are shown in Fig. 21 and Table 3. According to the figure, it can be concluded that the E_U decreases with increasing anneal temperature up to 400 °C. This can be explained by Fig. 1, 6 and 7, where crystallinity of the films was found to increase with increasing annealing temperature, resulting in reduction of dislocations, attributing to reduction of E_U of the fabricated films. However, the films annealed at 500 °C show slightly high value for E_U than the film annealed at 400 °C, potentially due to deterioration of the films annealed at 500 °C as discussed earlier.

3.4. Depth profile analysis

EDX spectroscopic measurements were employed in order to investigate the effect of annealing temperature on film composition along its cross section. Measurements were carried out under electron accelerating voltage of 10 kV. The Fig. 22 shows the variation of Cd and Te atomic compositions measured for thin films annealed at different temperatures. Compositional analysis was carried out at three different regions of the thin film along the cross section; near the film surface, close to the center of the film and near substrate.

According to the Fig. 22(a), it can be observed that thin film is Te rich near the surface at annealing temperatures below 400 °C. However, the center of the film looks predominantly Cd rich according to the Fig. 22(b). But close to the substrate, as can be seen in the Fig. 22(c), film becomes more Te rich and the Te richness looks to increase with increasing annealing

temperature. In this work, all the CdTe thin films were fabricated on glass substrates under a substrate temperature of 200 °C. Experiments on glass substrates have reported that the sticking coefficient of Te on glass is very close to 1.0 for substrate temperatures as high as 250 °C, while it is almost negligible for Cd on glass, even for substrate temperatures as low as 26 °C [59,60]. Hence the Te rich nature of the CdTe film close to the substrate observed in Fig. 22(c) can be because of the higher sticking coefficient of Te on glass compared to Cd on glass. During the recrystallization of thin films with increasing annealing temperature, more Te atoms can remain stuck to the substrate than Cd due to high sticking coefficient of Te compared to Cd on glass substrates. Therefore, it is possible to observe an increment in Te atomic percentage near the substrate with increasing annealing temperature as seen in Fig. 22(c).

4. Conclusion

Structural analysis of fabricated films revealed that the CdTe films are polycrystalline in nature with cubic zinc-blende structure. All characteristic 10 diffraction peaks of CdTe in the 2θ range of 10° to 100° were visible for films annealed at 300 °C and beyond. Crystallite size was found to increase with increasing annealing temperature suggesting better crystallinity. However, films annealed at 500 °C were found to demonstrate a non-uniform nature with voids on the surface according to the SEM images. Additionally, strong oxide peaks appearing in the GIXRD pattern suggests deterioration of the crystal at 500 °C. Therefore, both GIXRD and SEM analysis suggest films annealed at a temperature of 400 °C to be a better film.

All the transmittance spectra reveal interference effects for wavelengths beyond the absorption edge, suggesting uniformity in thickness. Refractive index, absorption coefficient, extinction coefficient, dielectric constants and relative density were found to be the highest for the film annealed at 400 °C. In addition, the obtained high optical conductivity for films annealed at 400 °C proposes high absorption of incident radiation. The Urbach energy calculations also indicate that the films annealed at 400 °C has low imperfections in the crystal lattice compared to the rest.

EDX results show that the composition of the CdTe film at different regions along the cross section can vary with the annealing temperature. According to the results, regions near surface and center of the film are slightly Te and Cd rich respectively. However, composition of

the regions near the substrate was found to become more Te rich with increasing annealing temperature. Accordingly, it can be observed that film composition throughout film can vary with changing annealing temperature.

This study suggests that changing the annealing temperature as a post deposition treatment affects structural and optical properties of CdTe thin film as well as its composition. According to the observations, films annealed at 400 °C can be concluded to be the best films for photovoltaic applications due to its superior optical and structural properties.

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Tables

Table 1

Variation of structural parameters with respect to annealing temperature.

Annealing Temperature (°C)	C_{III}	σ	a (Å)	D (nm)	δ ($\times 10^{11} \text{ cm}^{-2}$)	ε ($\times 10^{-4}$)
200	1.652	0.652	6.487	26.7	1.404	2.575
300	1.357	0.357	6.485	28.6	1.224	1.638
400	1.423	0.423	6.485	29.5	1.148	2.950
500	1.424	0.424	6.491	30.4	1.083	6.125

Tables

Table 2

Variation of (111) in-plane stress with respect to annealing temperature.

Annealing temperature (°C)	In-plane stress of (111) (MPa)
As-deposited	-556.7
200	-508.3
300	-333.1
400	-372.8
500	-284.0

Tables

Table 3

Optical parameters of CdTe thin films.

Annealing Temperature °C	E_g (ev)	n	α (cm ⁻¹)	k (×10 ⁻⁵)	ε_1	ε_2 (×10 ⁻⁵)	ρ	σ_o (×10 ⁹ s ⁻¹)	E_U (meV)
As-deposited	1.52	2.54	1.48	1.23	6.43	6.25	0.96	8.93	20.87
200 °C	1.51	2.56	1.54	1.29	6.54	6.58	0.96	9.39	19.82
300 °C	1.50	3.47	4.53	3.79	12.03	2.62	1.11	37.50	16.68
400 °C	1.50	3.52	4.71	3.93	12.40	2.77	1.12	39.54	16.27
500 °C	1.50	3.27	3.87	3.23	10.70	2.11	1.09	30.19	16.30

Figure 1

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