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Consequence of Post-Annealing on Optical, Structural and Electrical Properties of Cadmium Telluride Thin Films for Solar Cells Applications

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Abstract: In this paper, the thermally evaporated thin films of Cadmium Telluride (CdTe) have been deposited onto a highly cleaned glass substrate at pressure ~10^{-5} mbar. The thicknesses of CdTe thin films have been taken 1µm. After that, these thin films were placed in quartz glass tubes and annealed under a 500W halogen lamp for different times: 1 minute, 2 minutes, 3 minutes, and 4 minutes. The optical, structural and electrical properties have been carried out using UV-Vis-NIR, SEM, thermal electrical power (TEP) measurements, I-V and XRD measurements. In this study, it is shown that the optical and structural properties of CdTe thin films increase with increasing annealing time, while the electrical properties indicate the p-nature of CdTe thin films, suggesting that they can be used in solar cells as p-type absorber layers. Additionally, all essential conditions or requirements for improving the performance of solar cells were observed and mentioned.

Keywords: CdTe thin films; Annealing time; Thermal evaporation technique; Physical properties.

1 Introduction

Solar cell technology can overcome the increasing energy demand of the world. In this chain, the CdTe based thin film solar cells have been playing an important role in recent years. To increase the performance of solar cell annealing of CdTe is the key process. In this prospect, Punitha et al. [1] have developed CdTe thin films using the electron beam evaporation method onto an amorphous substrate and they introduced post-deposition heat treatment (annealing) process on CdTe. They have investigated the impact on the optical properties of the CdTe thin films. They have observed that the annealing process gives rise to the polycrystalline nature and the reduction in the optical energy band gap values. Asabe et. al. [2], have investigated the annealing effect on electrochemically grown CdTe thin films. The optical energy band gaps have been observed as direct band gaps and have been found to decrease their values from 1.64eV to 1.50eV with increasing annealing time. The optical result states that the polycrystalline natures of the thin films have recognized an increase with increasing annealing time. The SEM result states, the thin films have uniform, smooth and spherical grains with a crack-free surface. They have also observed the fill factor and power conversion efficiency values as 71 and 3.89% respectively. Kumar et. al. [3] has been investigated the effect of rapidly thermal annealing on CdSe thin film. They deposited CdSe thin films using the thermal vacuum evaporation technique under the pressure of 10^{-5} torr and rapid annealed the thin films at 60 and 120sec using a halogen lamp. They have also investigated that the energy band gap value decreases from 1.74 to 1.67eV with increasing annealing time. The other optical parameters like crystallinity, grain size and surface roughness increase with annealing. The impact of annealing on CdTe thin films has been studied by Garadkar et. al. [4], they have developed CdTe thin film on glass substrate using chemical bath deposition techniques. They have observed improvement in structural, optical and surface properties of the thin films with increasing annealing times. The effect of annealing on CdTe thin films has been investigated by Khan et. al. [5], they have developed CdTe thin film using a thermally evaporated method onto a soda lime glass substrate. They have observed the change in CdTe properties based on laser annealing treatment of these thin films. They have concluded that the laser 60J/pulse is the optimized laser output energy for the best results. The impact of rapid thermal annealing onto a thin film of ZnS has been studied by Kumar et. al. [6]. They formed a ZnS layer onto a cleaned glass substrate using the thermal vacuum evaporation method and rapid annealed the thin films using 500Watt halogen lamp for 30 sec and 60sec. The crystallinity of CdTe has been recognized as increasing and energy band gap values have observed decrease with annealing.

In this current study, we have grown CdTe thin films onto a cleaned glass substrate using thermal vacuum evaporation techniques. These thin films have been annealed for 1min to 4 minutes to observe the impact of annealing on structural, optical and electrical properties and for this, the UV-VIS-NIR, SEM, TEP, I-V and XRD measurements have been taken under investigation.

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2 Experimental techniques

2.1 Substrate cleaning process

It is the necessary and required process before every deposition. In this work, the glass substrate have been placed into Deionised(DI) water at 50° C for 15 minutes and then these glasses were put into Acetone for 15 minutes. Now these glass substrates have been placed into isopropyl alcohol (IPA) for 15 minutes and then placed into Acetone for 15 minutes to reduce contamination from the substrate surface. Later all the substrates dried using a hot drier and now the substrates have finally been ready for deposition.

2.2 Thin film preparation

The Cadmium telluride (CdTe) material in powder form has been bought from Alfa Aesar scientific agencies with a purity of 99.999%. To deposit thin films, the thermal vacuum evaporation technique has been applied. Before starting the deposition process the inner wall of the chamber has been cleaned using isopropyl alcohol (IPA) to reduce the impurity of the last deposition. Now all five cleaned glass substrates have been attached to the sample holder in the chamber and CdTe material in the powder form has been placed into the molybdenum boat and closed the chamber gate. Using rotary and diffusion pumps a vacuum of ~10^{-5} mbar has been generated in the chamber. Now by maintaining a current in the range of 25 to 30A, the thickness of 1µm has been achieved onto a substrate, detected by the thickness monitor attached in the chamber. Later these prepared thin films have been placed into a 500W halogen lamp for rapid thermal annealing for 1min, 2min, 3min and 4 minutes annealing, to investigate the optoelectrical properties of the prepared thin films.

2.3 Characterization of thin films

The UV-VIS-NIR spectrophotometer has been used in the wavelength range of 300 to 900nm, to observe the optical properties such as absorption, transmission, band gap and extinction coefficients. For the investigation of the surface roughness and structural properties, the Scanning electron microscope (SEM) has been used. To observe the nature of the thin films and Seebeck coefficients the thermal electrical power (TEP) measurements have been carried out. The electrical properties as current-voltage relation (I-V) have been observed using the keithley-234 unit. The crystallographic properties have been investigated using an X-ray diffractometer (XRD) in the range of $20^\circ < 2\theta > 80^\circ$ with wavelength $\lambda = 1.54056$ Å.

3. Result and Discussion

3.1 Optical observations

The optical parameters like absorption, extinction coefficients, transmission and optical energy band gap have been observed using a UV-VIS-NIR spectrophotometer in the wavelength range 300 to 900 nm. Fig. 1 represents the plot between absorption and wavelength for room temperature (RT), 1 min, 2min, 3min and 4minutes annealed, thin films of CdTe.

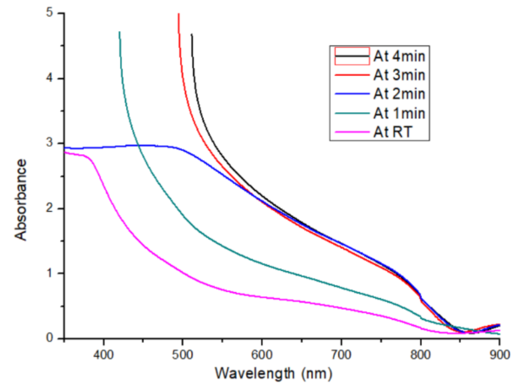


Fig. 1: Absorption versus wavelength for all the thin films

This plot clearly states that the absorptions have been found to increase their value as well as annealing time increasing from RT to 4 minutes. Also, near the 850 nm wavelength, the absorptions approached the same values and observed sudden dropped for all the thin films. This indicates the increase in crystallinity or grain sizes has been occurring with annealing the thin films. This may also indicate the energy band gap would be found near this wavelength and the optical energy band gap decreasing its value with annealing time. Tariq et. al. [7] have also observed the impact of annealing on the physical properties of CdTe thin films and they have found the same thing, the absorption has increased its value with increasing the annealing time.

Fig. 2 represents the transmission spectra of all thin films in the same wavelength range. This indicates that the transmission has been decreased with annealing time and similarly to absorption, the transmission has achieved almost similar value near the wavelength ~850nm for all thin films.

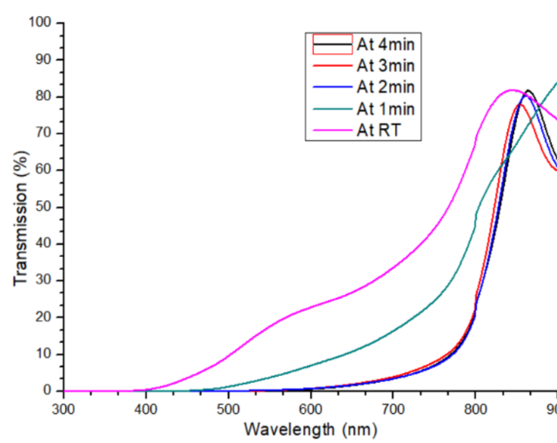


Fig. 2: The transmission versus wavelength curve for all the thin films of CdTe

These results fulfill and support the statement of the absorption spectrum. It also suggests the crystallinity or grain size and band gap have changed their values with increasing annealing time. The decrease in transmissions has also been observed by Metine et. al. [8], they have observed that by the healing effect the transmission decreases with annealing time. This is a good match and supportive data as this current study.

The optical energy band gap is an essential property of solar cells. All the solar cell properties and performance depend on the energy band gap. The energy band gap can be evaluated using Tauc's relation [9].

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

Here 'α' is used for the absorption constant, and 'n' represents a constant (It has a value ½ for direct and 2 for indirect band gap.

Fig 3 draws a plot between $(\alpha h\nu)^2$ and energy (hν), suggested by Tauc's, to evaluate the energy band gap. By taking the intercepts on hν axis, one can observe the energy band gap value using this curve.

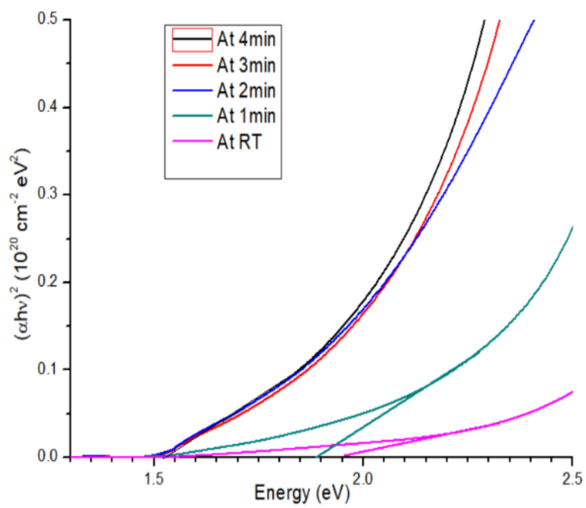


Fig. 3: Tauc's plot to evaluate energy band gaps

The observed energy band gap values as 1.95, 1.90, 1.53, 1.53 and 1.53 eV for CdTe thin films at RT, 1min, 2min, 3min and 4 min annealed respectively. Drastic changes in energy band gap have been recorded while annealing the thin films from RT to 1min and 1min to 2minutes annealing. And the other hand the band gap has found the same values for 2 min, 3min and 4minutes annealed thin films. The linearity of the curve indicates the transition is a direct allowed type of transition in all CdTe thin films. The changes in the energy band gap have been observed due to an increase in crystallinity and grain size of thin films. Kokate et. al. [10] have investigated the annealing impact on CdTe thin films and recognized that the energy band gap decreases with increasing annealing time as observed in our case. They have evaluated CdTe has changed their band gap from 1.64 to 1.50eV with annealing, the almost same value as in our case. This study is well matched and supportive of this work.

To investigate the scattering behavior of the photons by thin films, the extinction coefficients have been evaluated for all thin films. The extinction coefficients relation has been given as [11].

$$k = \frac{\alpha\lambda}{4\pi}$$

Where α is used for absorption coefficients.

The observed extinction coefficients value and wavelength curve was shown in Fig.4.

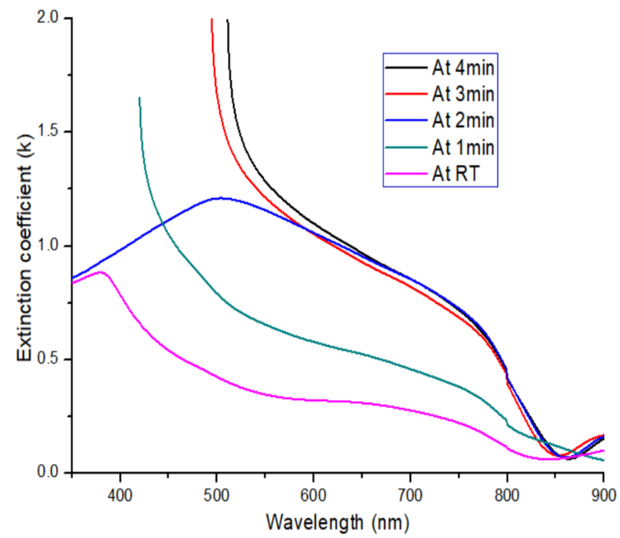
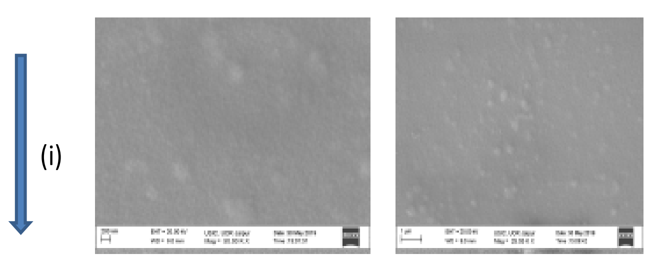


Fig. 4: The Extinction coefficients of CdTe thin films at different annealing times

The value of extinction coefficients has been increasing with annealing time. Hou et. al. [12] has investigated that for higher annealing temperatures the extinction coefficient value increases, which are well matches with our data. The increase in extinction coefficient indicates that the less photon scattered, or the absorption will be high for the thin films. This is in good agreement to improve the performance of solar cells.

3.2 Scanning Electron Microscope (SEM)

The SEM images of all the CdTe thin films have been taken from the top side of the thin films. The SEM images of all CdTe thin films as RT, 1min, 2min, 3min and 4minutes annealed, have been shown in Fig. 5 (i to v^{th} respectively).



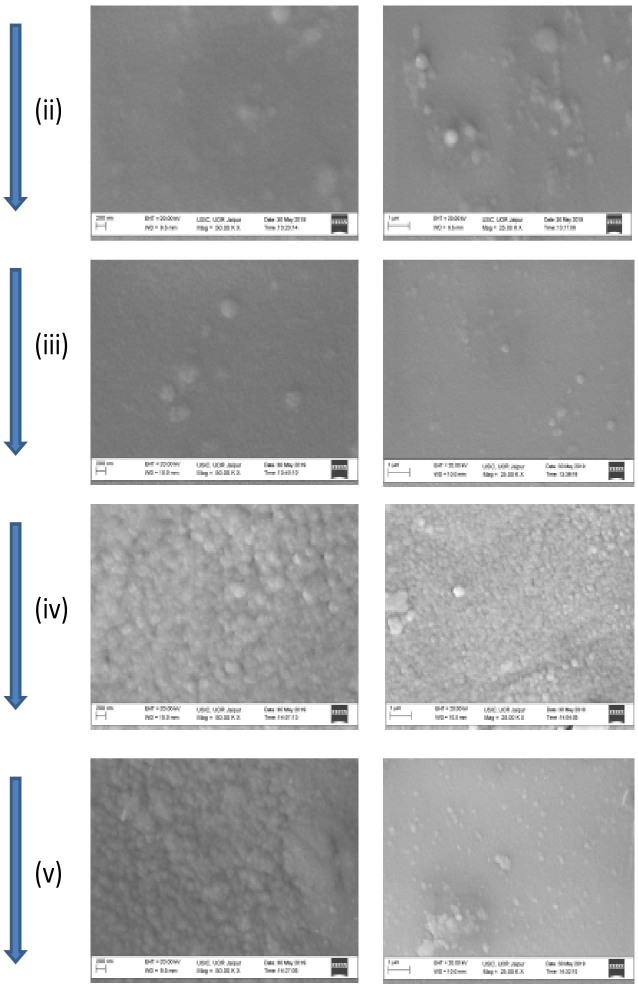


Fig. 5: The SEM images from RT to 4min annealing are shown in (i) to (v^{th}) respectively

These results clearly state that all the thin films have uniformly deposited, there is no pinhole found on the surface of the thin films. In the start, with CdTe thin films at RT, and there were very fewer grains recognized, but as well as annealing increased, the increase in gain growth can easily be seen in the SEM images. As well as going from (i) to (v^{th}) image we can clearly see the grain growth. The grains have found in small sizes in all thin films. The crystallinity has also been found to increase with an annealing time. The increase in grain size is resulting in an increase in a carrier lifetime or less probability of charge recombination will be found. Mathew et. al. [13] has observed that grain growth occurs with increasing annealing, this well matches the data with our result. The increase in grain growth is directly proportional to the increase in carrier lifetime time, so overall it will improve the performance of the solar cells.

3.3 Thermal electric power (TEP) measurement

To measure the majority charge carriers and Seebeck coefficient in thin films the thermal electrical power measurement has been under analysis. For this, the thin films have been placed in the TEP box, the schematic block diagram of the TEP box is shown in Fig. 6

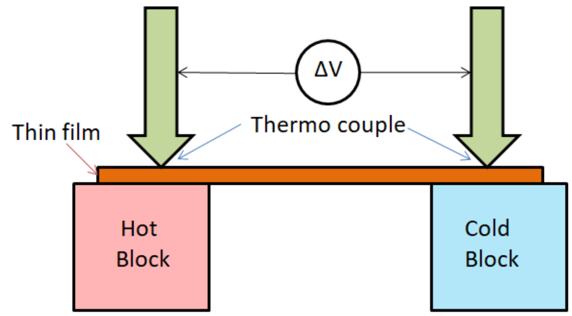


Fig. 6: The schematic diagram of TEP measurements

In this box there were two blocks, one is taken at constant pressure called a cold block and another is heated by an electrical heater called a hot block. The thin film has been placed onto these two blocks as shown image. The voltage differences between the two ends of the thin film have been observed with a temperature gradient, using a thermocouple attached to it. The graph between voltage difference and temperature gradient is plotted in Fig. 7, for all the thin films. The value of Seebeck coefficients has been measured using the relation below

$$S = \frac{\Delta V}{\Delta T}$$

The TEP observations have been taken for the temperature from 298 to 403K and evaluated the voltage gradient developed across it. The polarity of the voltage gradient has found a positive value. The holes are the majority charge carrier in CdTe thin films. That suggests this CdTe thin film can be used as a p-type absorber layer in solar cells. But polarity becoming negative for higher temperatures indicates the nature of thin films or negative majority charge carriers (electrons) were increasing with annealing time.

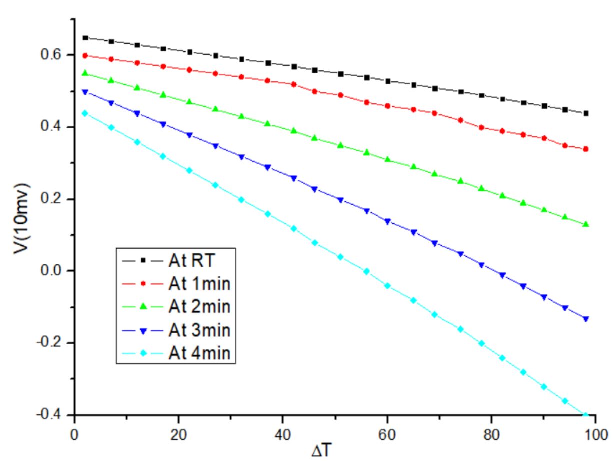


Fig. 7: The plot between voltage gradient versus temperature

Table 1: Evaluated various XRD parameters

Thin films	2θ (°C)	Miller indices	d Å	a Å	b Å	c Å	FWHM β (rad.)* 10^{-3}	D nm	ε* 10^{-4}	δx10^{14}m^{-2}	Nx10^{15}m^{-2}
CdTe	23.17	(111)	3.84	5.75	5.75	5.75	6.1	24.19	14.96	17.08	70.58
	38.73	(220)	2.32	3.48	3.48	3.48	2.61	58.62	6.18	2.90	4.96
	46.04	(311)	1.97	2.95	2.95	2.95	4.89	32.19	11.25	9.65	29.97

Also, the TEP plot has been found to decrease continuously for all the thin films, but it decreases abruptly for higher annealed thin films, as 4 min annealed thin films voltage gradient decreases fastest in all the thin films. The observed Seebeck coefficient values were recorded as 21, 29, 44, 60 and 78 μV/K for thin films RT, 1min, 2min, 3min and 4min annealed respectively. This may be due to an increase in free-charge carriers with annealing. Singh et. al. [14], has been observed that the abrupt decrease has recognized with the annealing time increasing the same as in our case. This is an essential condition for better performance of the solar cells.

3.4 Current-voltage characteristics

TheCurrent-voltage (I-V) relation has been observed using Keithley for all the thin films, in the voltage range -3 to +3 Volts. The I-V relation of the thin films has been represented in Fig. 8.

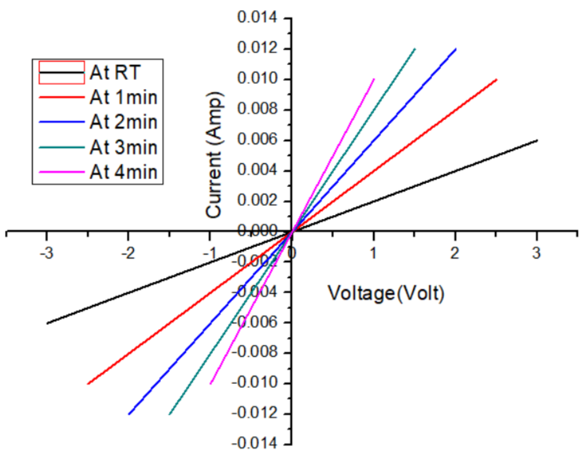


Fig. 8: Current-voltage characteristic of all the thin films

All the curves have been observed as linear, which indicates the ohmic nature of thin films. The curves also indicate that the conductivity has increased with annealing time. This may be due to an increase in free-charge carriers with annealing. This result also fulfills the TEP measurement results confirming that the number of charge carriers increase with increasing annealing time. Purohit et. al. [15] has observed the same result that, conductivity has been found to increase with annealing. That is in good agreement to improve the performance of the solar cell because increases in free charge carriers are the essential condition for the solar cells.

3.5 The crystallographic observation

The crystallographic structure of the pristine CdTe thin film has been investigated using an X-ray diffractometer (XRD). The recorded XRD pattern of the CdTe thin film has been shown in Fig. 9, having the preferred orientation along (111) plane at 2θ = 23.17°C and some additional peaks also found at 2θ values 38.73 and 46.04 corresponds to (220) and (311) planes respectively. The CdTe has been found in a cubic structure with cell parameter a= 5.57Å. Shaaban et. al. [16] have also observed the same planes, this is well matched and conformed to the CdTe thin film successfully deposited onto glass substrate as in our result.

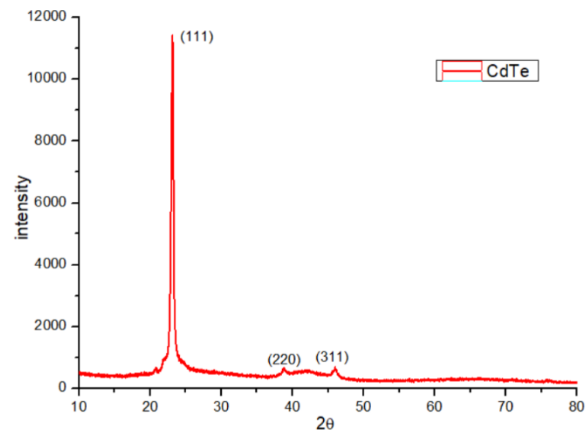


Fig. 9: The XRD pattern of the pristine CdTe thin film

The evaluated value of lattice constant (a), crystalline size (D), interplanar spacing (d), dislocation density(δ), internal strain(ε) and crystallinity per unit area (N) have been shown in Table 1.

The higher value of crystalline size indicates that this deposition technique is best to develop CdTe thin films because grain or crystalline size is directly connected with recombination lifetime and free charge carriers, which play a very important role in the performance of solar cells.

4. Conclusion

CdTe thin films were grown onto a cleaned glass substrate by vacuum evaporation technique. The optical result has confirmed that they directly allowed energy bands to have formed having values from 1.95 to 1.53eV for RT to 4minutes annealed respectively. The decrease in energy band gaps indicates the increase in crystallinity or grain size. By increasing the extinction coefficient, less scattering of photons occurs and more photons are absorbed by the thin films. The SEM result indicates an increase in grain size or crystallinity with no pin holes and uniformly deposited thin films. That means the free charge charier increases with a high recombination lifetime. The thermoelectric power measurements and positive value of the Seebeck coefficient indicate that the majority of charge carriers were holes. Increasing temperature gradients result in the majority of charge carriers becoming negative or electrons. The current voltage characteristic shows an increase in conductivity or free charge carriers with annealing time. This result fulfills and supports the TEP results. The XRD result shows the CdTe having a cubic structure with cell parameter a= 5.57Å and crystalline size D= 24nm with preferred orientation along (111) planes. This study provides and confirms that annealing is the key process to modifying the optical, structural and electrical properties of the CdTe thin films. These properties can be modified by annealing to approach the ideal condition for high-performance solar cells.

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