Chalcogenide Letters Vol. 10, No. 6, June 2013, p. 209 - 216

INVESTIGATIONS ON OPTOELECTRONIC PROPERTIES OF DC REACTIVE MAGNETRON SPUTTERED CdTe THIN FILMS

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In the present work two individual metallic targets of Cd and Te were used for the deposition of CdTe thin films on mica substrates from room temperature to 300 °C by DC reactive magnetron sputtering method. XRD patterns of CdTe exhibit peaks at $2\theta = 27.7^{o}$, 36.2^{o} and 45.1^{o}, which corresponds to reflection on (2 0 0), (2 2 0) and (3 1 1) planes of CdTe cubic structure, respectively. The conductivity of CdTe thin films measured from four probe method decreases with the increase of substrate temperature. The activation energies (ΔE) of CdTe thin films are also found to be decrease with the increase of substrate temperature. These results may be correlated with Te excess that is greater in respective CdTe films. Optical transmittance spectra of CdTe thin films have a clear interference pattern in the longer wavelength region. The films have good transparency (T > 85 %) exhibiting interference pattern in the spectral region between 1200 – 2500 nm. The optical band gap of CdTe thin films are found to be in the range of 1.48 – 1.57 eV. The refractive index, n decreases with the increase of wavelength, λ. The value of n and k increases with the increase of substrate temperature.

(Received May 11, 2013; Accepted June 22, 2013)

Keywords: Thin films, DC reactive magnetron sputtering, Electrical properties, Optical properties

1. Introduction

Cadmium telluride (CdTe) is a promising photovoltaic material for thin-film solar cells because of its near-optimum bandgap of ~1.5 eV and its high absorption coefficient. Small-area CdTe cells with efficiencies of more than 16% and commercial-scale modules with efficiencies of 11% have been demonstrated [1, 2]. However, the performance of CdTe cells has been limited by the conventional polycrystalline CdS/CdTe device structure. The CdTe thin-film solar cell has a large absorption coefficient and high theoretical efficiency. Moreover, large-area photovoltaic panels can be economically fabricated. These features potentially make the CdTe thin-film solar cell the leading alternative energy source. However, the record CdTe efficiency (16.5%) is much less than its theoretical maximum efficiency (29%), primarily because the open-circuit voltage (0.845 V) is well below what is expected for its band gap (1.5 eV). The incorporation of an electron reflector is a strategy to improve the open-circuit voltage of solar cells, and thus a strong possibility to improve the efficiency of CdTe thin-film solar cells. An electron reflector is a conduction-band energy barrier at the back surface of the solar cell, which can reduce the recombination due to the electron flow to the back surface [3, 4]. The development of cells with a much thinner CdTe layer (<1 μm, which we call ultra-thin) would help to extend Te supplies and would have additional advantages in manufacturing such as reduced materials cost, higher throughput, easier cell isolation and interconnections, lower use of toxic materials and reduced waste treatment cost.

Various methods such as hot wall vacuum evaporation, close-spaced sublimation, molecular beam epitaxy, electro-deposition, etc. have been used to prepare CdTe films [5]. Among them DC magnetron sputtering has been regarded as one of the most attractive and effective

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fabrication techniques in the mass production of films. In this paper, a systematic study on optoelectronic properties of CdTe thin films at different substrate temperatures has been discussed.

2. Experimental details

DC reactive magnetron sputtering method is employed in the present investigation for the deposition of CdTe thin films. The sputtering targets of size 2 inch diameter and 4 mm thickness of Cd (99.99% purity) and Te (99.99% purity) were used in the present study. Pure argon used as sputter gas was admitted into the chamber through mass flow controllers (Model GFC 17, Aalborg, Germany). The sputtering deposition of CdTe thin films by using individual metallic targets of Cd and Te are shown in Fig 1. The deposition conditions for CdTe thin films are shown in Table 1.

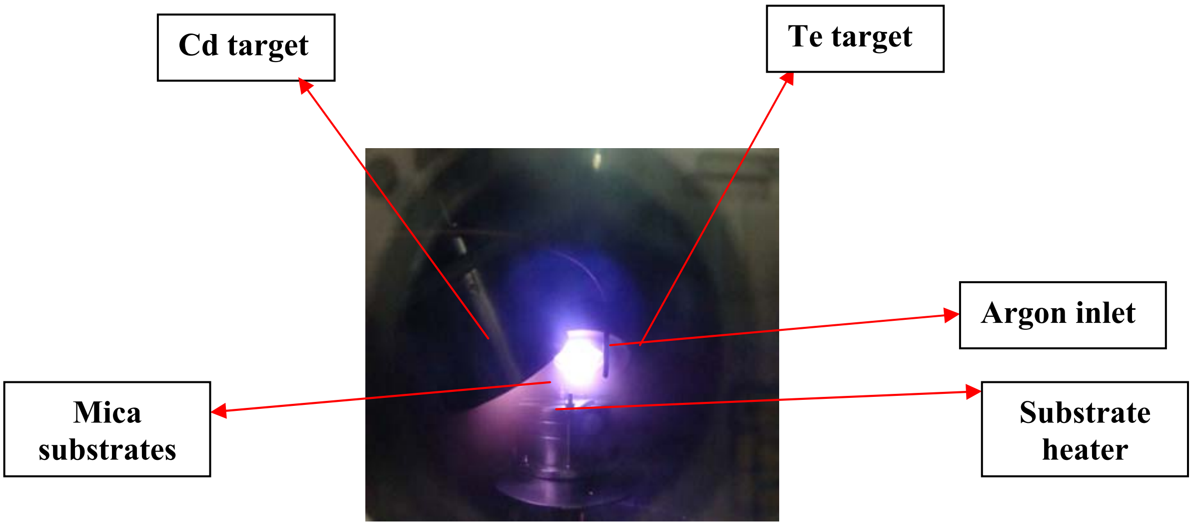

Fig 1. DC reactive magnetron sputtering process of CdTe thin films

Table 1. Sputtering deposition parameters for CdTe thin films

Sputtering target	: Cd (99.99%) and Te (99.99 %) (2 inch diameter and 4 mm thickness)
Substrate	: Mica
Base pressure	: 6 x 10^{-4} Pa
Substrate temperature	: RT (30 °C) - 300 °C
Sputtering pressure	: 0.3 Pa
Argon flow rate	: 30 sccm
Deposition time	: 20 min
Deposition rate	: 0.18 nm/s
Sputtering power of Cd target	: 105 W
Sputtering power of Te target	: 80 W

3. Results and discussion

Fig. 2 shows the XRD patterns of CdTe thin films deposited on mica substrates exhibits peaks at $2\theta = 27.7^{o}$, 36.2^{o} and 45.1^{o}, which corresponds to reflection on (2 0 0), (2 2 0) and (3 1 1) planes of CdTe cubic structure, respectively. The intensities of XRD patterns increase with increase of substrate temperature upto 150 °C and then it decreases at higher substrate temperatures. The average crystallite size (D) of CdTe thin films was determined from the Scherer formula. The structural parameters of CdTe thin films are tabulated in Table 2. The lattice constant and d-spacing values increase with the increase of substrate temperature.

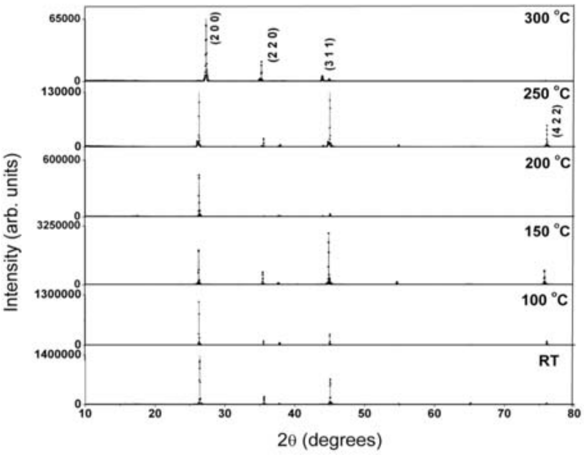

Fig. 2 XRD patterns of CdTe thin films

Table 2. Structural parameters of CdTe thin films

S.No	**Substrate temperature (^oC)**	**2θ (degrees)**	**FWHM, β (degrees)**	**(h k l)**	**d - spacing (nm)**	**Lattice constant, a (nm)**	**Crystallite Size, D (nm)**
1	RT	26.40	0.07	(2 0 0)	0.3374	0.6748	20.33
2	100	26.25	0.06	(2 0 0)	0.3391	0.6782	23.72
3	150	26.30	0.05	(2 0 0)	0.3385	0.6770	28.47
4	200	26.30	0.06	(2 0 0)	0.3386	0.6772	23.72
5	250	26.25	0.05	(2 0 0)	0.3392	0.6784	28.46
6	300	26.29	0.06	(2 0 0)	0.3386	0.6772	23.72

It is well known that the electronic transport properties of the polycrystalline thin films strongly depend on their structure [6]. The study of the temperature dependence of electrical conductivity of such films offers a lot of information on the electrical conduction mechanism in respective films in correlation with their structure. The conductivity (σ) varies with the temperature according to the relation

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{1}$$

which is in concordance with the thermally activated conduction mechanism. ΔE denotes the thermal activation energy of electrical conduction, σ_o represents a parameter depending on the semiconductor nature and k_B is the Boltzmann's constant. It is seen from the Fig. 3 that for all the films the conductivity is a linear function of the reciprocal temperature, decreases with the increase of substrate temperature. Linearity of the plot is nearly same for all the films. The activation energy is evaluated from the slope of ln σ versus 1000/T (K^{-1}) plot in the higher temperature range. The activation energy values decreases with the increase of substrate temperature given in Table 3.

The decrease of ΔE is determined by increase of substrate temperature. These results may be correlated with Te excess that is greater in respective CdTe films. The segregation of tellurium excess in such films may determine the decrease of potential barrier in the grain boundary region and hence a decrease of ΔE. This can be explained by the role played by the free Te atoms in CdTe lattice like the acceptor impurities in p type semiconductors. An increase of the Te amount will determine an increase of carrier concentration [7, 8]. Similar behavior was reported in literature for CdTe thin films deposited using thermal evaporation [9, 10] and close-spaced sublimation (CSS) techniques [11].

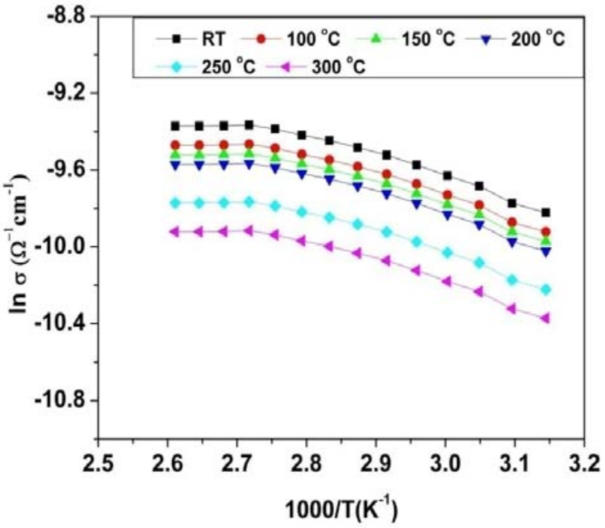

Fig. 3 Temperature dependence of electrical conductivity for CdTe films

Table 3. Electrical properties of CdTe thin films

S.No	**Substrate Temperature (^{o}C)**	**Electrical conductivity, σ (Ω^{-1} cm^{-1})**	**Activation energy ΔE (eV)**
1	RT	8.54 x 10^{-5}	0.81
2	100	2.31 x 10^{-6}	0.80
3	150	6.54 x 10^{-6}	0.78
4	200	8.72 x 10^{-6}	0.77
5	250	3.14 x 10^{-7}	0.74
6	300	4.12 x 10^{-7}	0.71

The thermoelectric power (TEP) measurements were carried out for CdTe thin films using variable temperature method. In this method, the temperature of one end varied and temperature of another end fixed and induced e.m.f. was observed. The thermoelectric power was calculated using the formula given below

$$s = \frac{\Delta V}{\Delta T} \quad \mu V/K \qquad (2)$$

where ΔT is temperature gradient and ΔV is thermo e.m.f. at absolute temperature.

The temperature dependence of thermoelectric power is shown in Fig. 4 for CdTe thin films at different substrate temperatures. The negative sign of TEP suggests that conduction should occur predominantly due to electrons, which established the n-nature of the CdTe thin films. The drop of TEP with increase of temperature indicates that the electrons are excited into conduction band, which yield minor contribution to the charge transport process. The negative TEP at temperature reveals that the sample goes into n-type semiconductor and therefore the electrons in the conduction band mainly contribute to the charge transport process.

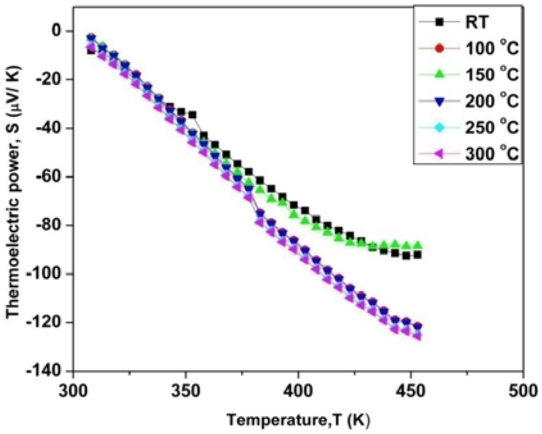

Fig. 4 Temperature dependence of thermoelectric power for CdTe films

It is observed that the value of E_0 varies with substrate temperature. It is well known that the value of maximum activation energy would be half of the forbidden energy. The forbidden energy of CdTe crystal is 1.5 eV as reported previously [12, 13]. The activation energy obtained in this study is comparable to the half of the forbidden energy of CdTe crystal. The value of activation energy ($E_0 >> k_BT$) obtained in this study indicates the deep level localized states in the forbidden energy.

From the thermoelectric measurements, S, the free charged carrier concentration, n was calculated according to the following equation [14, 15]

$$n = 2\, M^{3/2}\, [\, (\exp (2\, k_B + S) / k_B)\,] \tag{3}$$

$$M = [2\pi\, m^* k_B T/h^2]$$

where m* is the effective mass, which was taken as $0.11m_e$, and h is Planck's constant. The carrier concentration increases from 3.14×10^{16} cm^{-3} to 6.84×10^{16} cm^{-3} with increase of substrate temperature. The values of carrier concentration of CdTe thin films are tabulated in Table 4.

Table 4. Thermoelectric properties of CdTe thin films deposited on mica at different substrate temperatures

S.No	**Substrate Temperature (°C)**	**Thermoelectric power , S (μVK^{-1})**		**Carrier concentration, n (cm^{-3})**
		313 K	**453 K**	
1	RT	8.6	92.0	3.14×10^{16}
2	100	6.5	121.5	4.22×10^{16}
3	150	6.4	88.4	5.12×10^{16}
4	200	7.0	122.0	6.72×10^{16}
5	250	10.0	125.0	6.84×10^{16}
6	300	10.5	125.5	6.84×10^{16}

Optical transmittance spectra of CdTe thin films deposited on mica is shown in Fig. 5. A clear interference pattern is observed in the longer wavelength region. The films have good transparency (T > 85%) exhibiting interference pattern in the spectral region between 1200 – 2500 nm and display a clear explicit absorption edge interrelated to the optical bandgap. The absorption coefficient as a function of photon energy was determined by envelope function model [16-18]. Fig. 6 shows the variation of absorption coefficient (α) with photon energy (hν) for CdTe thin films

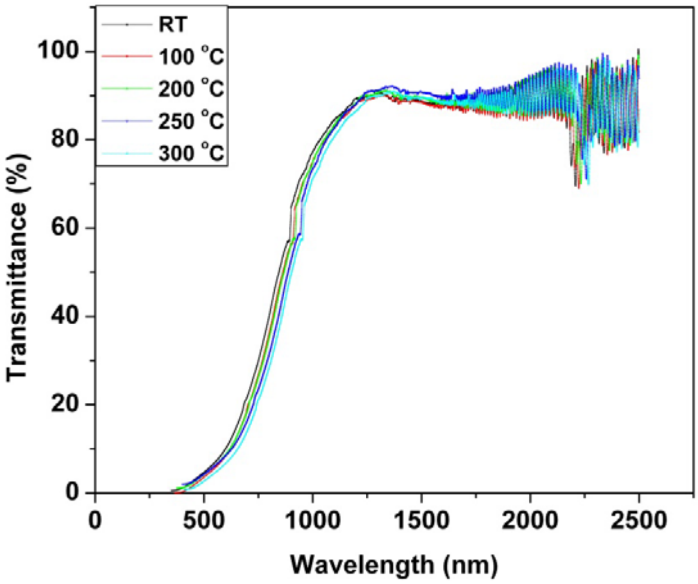

Fig. 5 Optical transmittance spectra for CdTe thin films

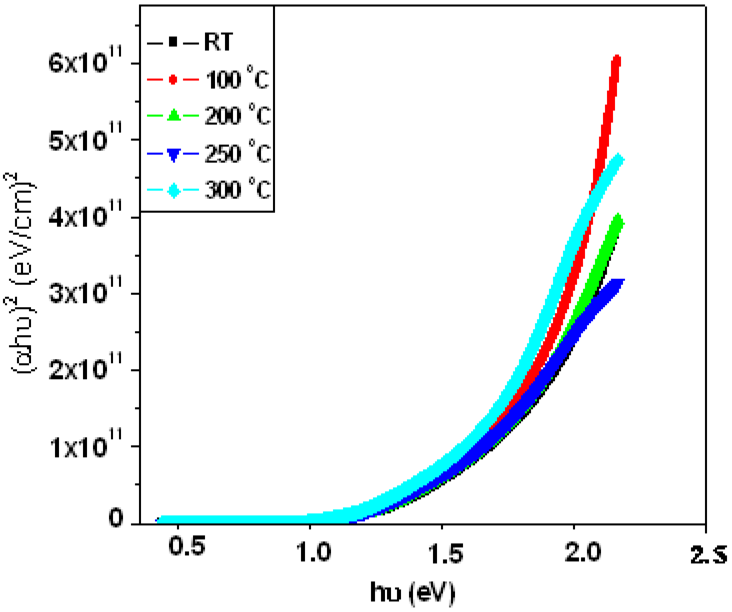

Fig. 6 Variation of $(\alpha h\nu)^2$ with photon energy (hν) for CdTe thin films

The shift observed at absorption edge towards lower photon energies for the heat treated layers could be attributed to the change in the grain size and the stoichiometry due to loss of Cd resulting formation of shallow acceptor levels [19, 20]. Fig. 6 shows the plot between $(\alpha h\nu)^2$ with photon energy (hν) for CdTe thin films deposited at different substrate temperatures. The optical band gap of CdTe thin films are found to be in the range of 1.48 – 1.57 eV. The bandgap value of heat treated layers was also found to be in good agreement with those published in the literature for bulk CdTe [21-23].

Optical constants such as absorption coefficient (α), extinction coefficient (k) and refractive index (n) for CdTe polycrystalline thin films is calculated from the equations reported in the previous literature [24]. The refractive index is determined using the method of recording envelopes around the interference maxima and minima in the transmittance spectra. Table 5 shows the optical constant values of CdTe thin films deposited on mica at different substrate temperatures.

Table 5. Optical constants of CdTe thin films deposited on mica at different substrate temperatures

S.No	**Substrate Temperature (^{o}C)**	**Absorption coefficient at 850 nm (α) cm^{-1}**	**Extinction coefficient at 850 nm (k)**	**Optical band gap E_g (eV)**
1	RT	5.96×10^{5}	0.040	1.57
2	100	5.52×10^{5}	0.037	1.54
4	200	4.95×10^{5}	0.033	1.51
5	250	4.85×10^{5}	0.032	1.49
6	300	4.36×10^{5}	0.029	1.48

Fig. 7 shows the variation of refractive index with wavelength for CdTe thin films deposited on mica at different substrate temperatures. It is observed from these graphs of n vs λ that the refractive index, n decreases with the increase in the wavelength, λ. The refractive index increases with increase of substrate temperature from room temperature to 300 ^{o}C. Similar results were found in CdTe thin films deposited by thermal evaporation method [25].

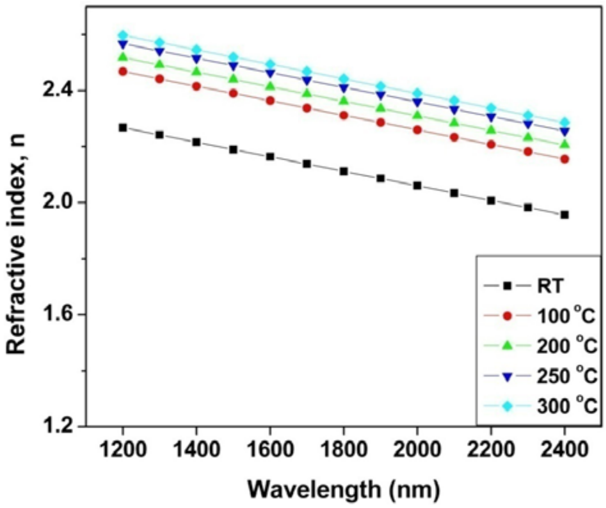

Fig. 7 Variation of refractive index with wavelength for CdTe thin films

4. Conclusions

CdTe thin films have been grown by DC reactive magnetron sputtering technique on mica substrates by varying substrate temperature from room temperature to 300 ^{o}C. The films have a preferred crystalline orientation of (0 0 2) direction. From the electrical measurements, the conductivity and activation energy decreases with the increase of substrate temperature. These results are correlated with Te excess that is greater in respective CdTe films. Optical transmittance spectra of CdTe thin films deposited on mica have a clear interference pattern in the longer wavelength region. The films have good transparency (T > 85%) exhibiting interference pattern in the spectral region between 1200 – 2500 nm. Refractive index (n) of CdTe thin films increases with the increase of substrate temperature. From the results we conclude that these films satisfy the basic requirement for the thin-film solar cells.

Acknowledgements

The authors are thankful to UGC, New Delhi, India for financial support under the major research project (F.NO.37-346/2009, SR).

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