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Optical properties of thermally evaporated cadmium telluride thin films

U.P. Khairnar*, D.S. Bhavsar, R.U. Vaidya, G.P. Bhavsar

Thin Film Laboratory, Department of Physics, Pratap College, Amalner 425401, Jalgaon District, Maharashtra, India

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Abstract

Polycrystalline CdTe films have been deposited onto glass substrates at 373 K by vacuum evaporation technique. The transmittance and reflectance have been measured at normal and near normal incidence, respectively, in the spectral range 200–2500 nm. The dependence of absorption coefficient, α on the photon energy have been determined. Analysis of the result showed that for CdTe films of different thicknesses, direct transition occurs with band gap energies in the range 1.45–1.52 eV. Refractive indices and extinction coefficients have been evaluated in the above spectral range. The XRD analysis confirmed that CdTe films are polycrystalline having hexagonal structure. The lattice parameters of thin films are almost matching with the JCPDS 82-0474 data for cadmium telluride.
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Keywords: Thermal evaporation; Optical properties; Band gap; XRD

1. Introduction

Cadmium telluride is considered at present one of the most promising materials, for device applications. It has high absorption coefficient in the visible range of the solar spectrum and its band gap is close to the optimum value for efficient solar energy conversion [1,2]. The material can be prepared in n-type and p-type forms so that solar cells can be formed in both homojunction and heterojunction configurations. A survey of the literature shows that different techniques of deposition have been developed to obtain device grade CdTe thin films, among which electrodeposition [3], rf sputtering [4], closed vapor transport [5], spray pyrolysis [6], screen printing [7], and vacuum evaporation [8,9] are worth mentioning. All these techniques have their own merits and demerits in producing high quality CdTe films. Recently several workers have studied structural characteristic and optical properties depending on the deposition conditions [10–17]. Most of these investigations did not deal with each deposition condition, separately and some contradictions appeared in the results. Therefore in this work systematic investigation of the effect of the preparation conditions on the optical properties and structural characteristic has been carried out. An interpretation of the determined optical constant variations in correlation with the corresponding structural parameters is presented.

2. Experimental

2.1. Deposition of CdTe films

A series of CdTe films have been deposited via sublimation of the compound in vacuum higher than 10^{-5} mbar under controlled growth conditions of various thicknesses. Cadmium telluride material used was in powder form. This was of “Aldrich Chemical Co.” make having purity of >99.99%. The substrates used were glass slides of dimensions 75 mm × 25 mm × 1 mm. The glass slides were cleaned with warm dilute chromic acid, detergent solution, distilled water and isopropyl alcohol in that order. All samples of different thicknesses (500, 1000, 1500, 2000, 2500, 3000 Å) were deposited under almost the same environment. The thicknesses of films were controlled by using quartz crystal thickness monitor model no. DTM-101 provided by Hind-High Vac. The deposition rate was maintained 10–15 Å s^{-1} constant throughout the sample preparations. The source to substrate distance was kept constant (10 cm) and substrate was kept at constant temperature (373 K). Deposited samples were kept under vacuum overnight.

2.2. Characterization of the films

The structural characteristics have been studied by X-ray diffractograms (Rigaku, Miniflex Japan) with Cu Kα radiation (1.5418 Å). The optical studies were performed in the wavelength range of 200–2500 nm. A double beam

* Corresponding author.
E-mail address: upkhairnar@rediffmail.com (U.P. Khairnar).

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spectrophotometer, Hitachi-330 Japan, was used for this purpose. The absorption coefficient, types of transition, optical constant and optical band gap were determined from these studies for all the evaporated thin films.

3. Results and discussion

The degree of preferred orientation was assessed by the "ratio" between the peak intensity of (1 0 0) to that of (1 0 1) reflections on the same scale. The full width at half-maximum (FWHM) was determined to a high degree of precision by a graphical computer program. The X-ray showed that all the films prepared were polycrystalline with a hexagonal structure.

The reflectance and transmittance spectra of these samples were recorded using Hitachi spectrophotometer model-330 in the spectral region 200–2500 nm. Using these data, the absorption coefficient α has been calculated by applying the relation:

$$\alpha = \frac{2.303}{d} \ln\left(\frac{1}{T}\right) \quad (1)$$

The absorption coefficient can be written in general form as a function of incident photon energy $h\nu$ as [18]

$$\alpha h\nu = A_0(h\nu - E_g)^P \quad (2)$$

where P has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect, and allowed or forbidden. In the direct and allowed cases $P = 1/2$, whereas for the direct but forbidden cases it is 3/2. But for the indirect and allowed case $P = 2$ and for the forbidden cases it will be 3 or more. And the constant A_0 is given by

$$A_0 = \left[\frac{e^2}{neh^2 m_e^*}\right](2m_r)^{3/2}$$

where m_e^* and m_r are the effective and reduced masses of charges carriers, respectively. E_g is the optical band gap, the value of P determined the nature of optical transition. The results have been analyzed according to relation (2).

Optical constants, refractive indices and extinction coefficients, have been evaluated from the reflection data and using the following relations [19]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

and

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

Absorption coefficients have been evaluated using percentage transmittance data as a function of wavelength presented in Fig. 1 for the samples of different thicknesses. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is presented in Fig. 2. This figure shows clearly the linear dependence for the value of $P = 1/2$. This is attributed to an allowed and direct transition with direct band gap energies. The evaluated band gap energies are 1.45, 1.49 and 1.50 eV for the samples of thicknesses 1560, 2000, and 2500 Å, respectively, clearly indicating dependence on thicknesses of films.

It was attempted to plot $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the samples of different thicknesses. These plots did not show any linear dependence indicating that the transitions are direct.

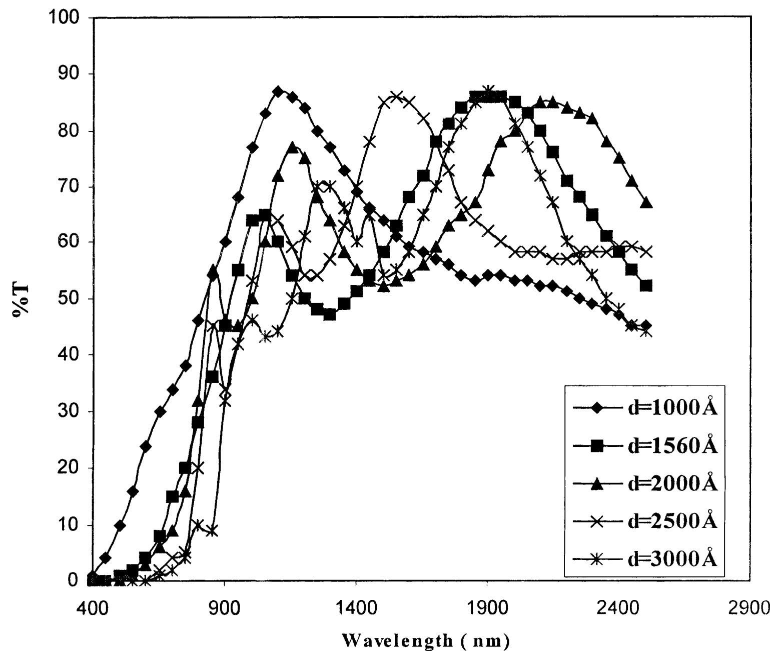

Fig. 1. Spectral behavior of transmittance of CdTe thin films of different thicknesses.

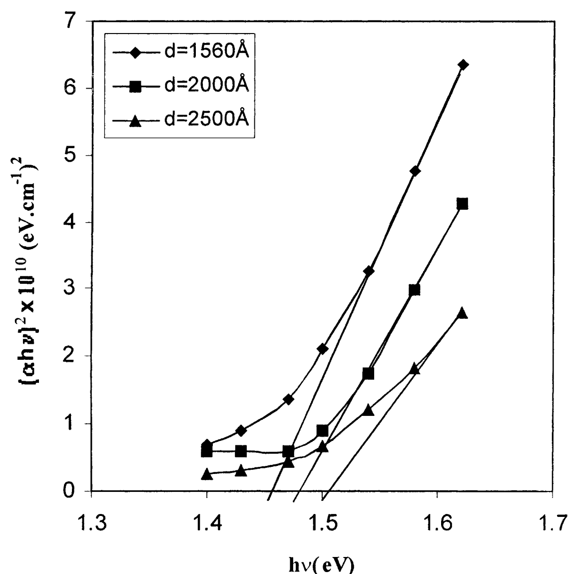

Fig. 2. Variation of $(\alpha h\nu)^2$ with photon energy for different thicknesses.

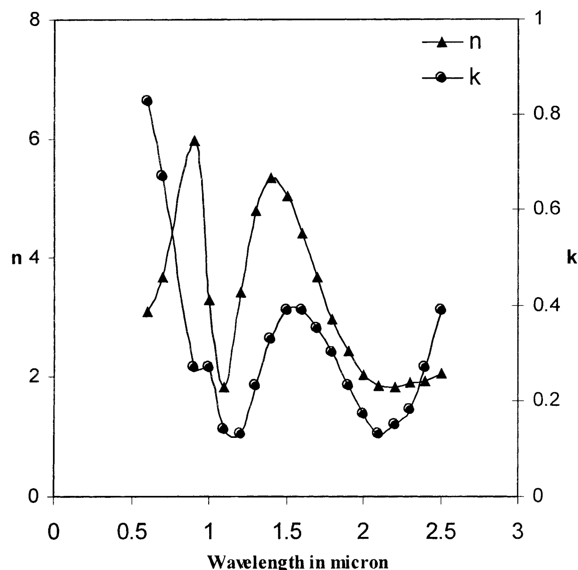

Fig. 3. Variation of n and k with wavelength ($d = 2000$ Å).

The optical transition observed by different workers [13–15,20,21] is more or less in agreement with one another as far as the gap width of approximately 1.5 eV is concerned. However as far as the character of the transition is concerned, some authors found it to be direct, while others found it to be direct and indirect with similar and different values. It is found that our results confirm only direct character of the optical transition. Our values for the direct gap width are consistent with previous findings for thin films [12,14,15,20], for single crystal [22,23], while other authors [16,17,24,25] reported higher values. This may attribute to the appearance of different phase of structural form of CdTe as revealed by XRD.

It is however difficult to account for the observed band gap shift as a function of thickness. The possible causes of the observed band gap shift may be accounted for one or more of the following mechanisms:

1. A hexagonal to cubic phase transformation taking place at higher temperature can reduce the energy gap of the film [17]. This is known for some II–VI compounds that exhibit the two phases [25].
2. Defect-induced absorption caused by incomplete transformation of metastable hexagonal to cubic phase [25].
3. Presence of a quantum size effect originated by the microstructure nature of the films with average grain sizes <300 Å [26,27].
4. Change in stoichiometry due to loss of Cd with heat treatment, which reduces the value of the energy gap [28].

In the present work, all the film samples investigated are of single phase of hexagonal structure. Therefore the first two mechanisms cannot account for the observed gap shift. Observed gap broadening may be accounted for by the third mechanism. As estimated crystallite sizes for all the samples of different thicknesses are less than 100 Å it may account by third mechanism i. e. presence of quantum size effect originated by the microstructure nature of the films. It is obvious that films of small thicknesses are more strained, have small size crystallites and are weakly oriented which together lead to highly absorbing films.

The variation of refractive indices and extinction coefficients as a function of wavelength is represented in Figs. 3–5, respectively, for the thicknesses 2000, 2500 and 3000 Å. From these figures it is found that variations in refractive

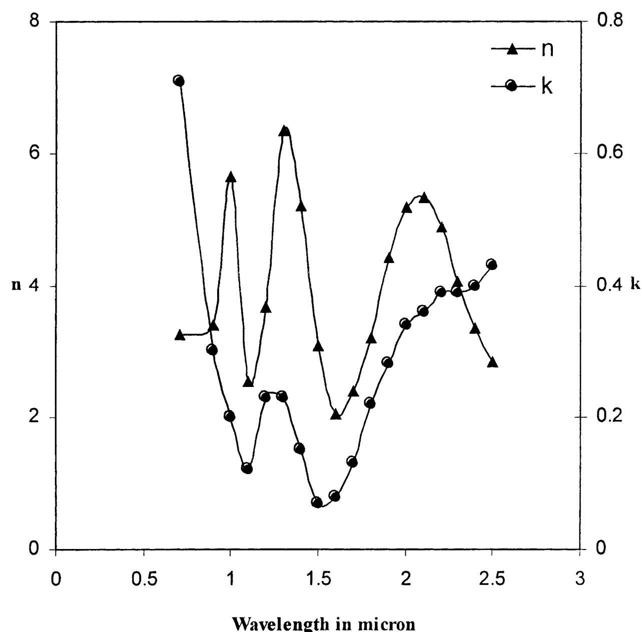

Fig. 4. Variation of n and k with wavelength ($d = 2500$ Å).

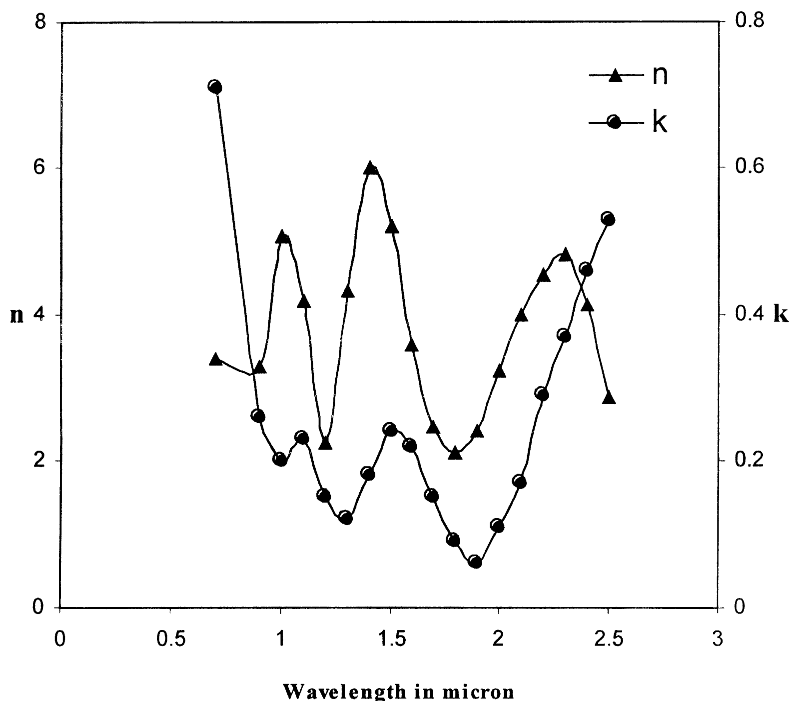

Fig. 5. Variation of n and k with wavelength ($d = 3000$ Å).

indices and extinction coefficient are oscillatory in nature. It is also found that the number of maxima and minima depend upon the thickness of the film samples. This comparative study reveals the following facts:

1. For the thinnest sample of thickness 500 Å, there is no well-defined maxima or minima in variation of n and k as a function of wavelength.
2. For the sample of thickness 1000 Å there are two well-defined maxima and one minima in the variation of n, while there is only one minima in the variation of k.
3. For the sample of thickness 1500 Å there are two minima and one maxima in the variations of n and k as a function of wavelength.
4. In the case of the sample of thickness of 2000 Å there are two well-defined maxima and one minima in the variation of n as a function of wavelength. While there are two well-defined minima and one maxima in the variation of k as a function of wavelength.
5. In the samples of higher thicknesses of 2500 and 3000 Å, the nature of variation of n and k as a function of wavelength, is similar having three well-defined maxima and

Table 1
Well-defined maxima and minima on variation of n and k

Serial no.	Sample thickness (Å)	Maxima			Minima		
		λ (μm)	n	k	λ (μm)	n	k
1	2000	0.900	5.95	–	1.100	1.820	–
		1.400	5.32	–	2.100	1.840	–
		1.000	–	0.28	1.000	0.000	0.14
		1.500	–	0.39	2.100	0.000	0.14
2	2500	1.000	5.64	–	1.000	2.520	–
		1.300	6.32	–	1.600	2.060	–
		1.200	–	0.24	2.500	2.860	–
		2.200	–	0.40	1.100	–	0.13
					1.500	–	0.08
3	3000	1.100	5.61	–	1.200	2.260	–
		1.400	5.98	–	1.800	2.120	–
		2.200	4.52	–	2.500	2.880	–
		1.100	–	0.24	1.300	–	0.12
		1.500	–	0.24	1.900	–	0.08

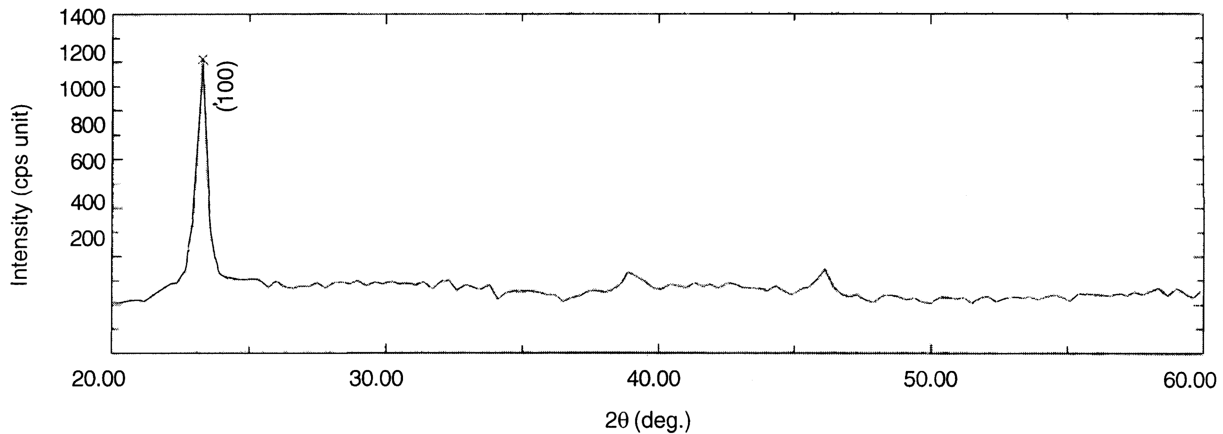

Fig. 6. X-ray diffractogram of as-deposited CdTe thin film of 2000 Å thickness.

two minima in the variation of n, while there are two well-defined minima and one maxima in the variation of k.

Refractive index varies in the range from 2 to 6 while the range of variation of extinction coefficient is from 0.1 to 0.7. This is represented in Table 1.

Myers et al. [20], and El-Shazly and El-Shair [12] reported the range of variation of refractive indices from 2.70 to 3.10 and the range of variation from near 0 to 0.5 for extinction coefficient for CdTe films deposited at different temperature. It therefore reveals that present results seems to be consistent for the extinction coefficient while for index of refraction the range of variation is much wide. This may be attributed to the particular structure of films and their thicknesses.

The XRD of typical CdTe film of thickness of 2000 Å and as-deposited film is presented in Fig. 6 and that of annealed samples of thickness 2000 and 2500 Å are presented in Fig. 7(a) and (b), respectively. From these X-ray diffractograms, it is observed that the main features of the diffractions patterns are the same but the peak intensity is varied. The peak intensity of the prime peak observed at $2\theta = 23.300$ in Fig. 6 of as-deposited sample of thickness 2000 Å is of the order of 1200 cps while that of annealed sample (annealing temperature = 573 K and annealing time = 6 h), the peak intensity of the prime peak observed at the same $2\theta = 23.300$ is of the order of 2000 cps. While the peak intensity of the same prime peak observed at $2\theta = 23.300$ for an annealed sample of thickness 2500 Å is of the order of 5000 cps. This observed peak is identified as

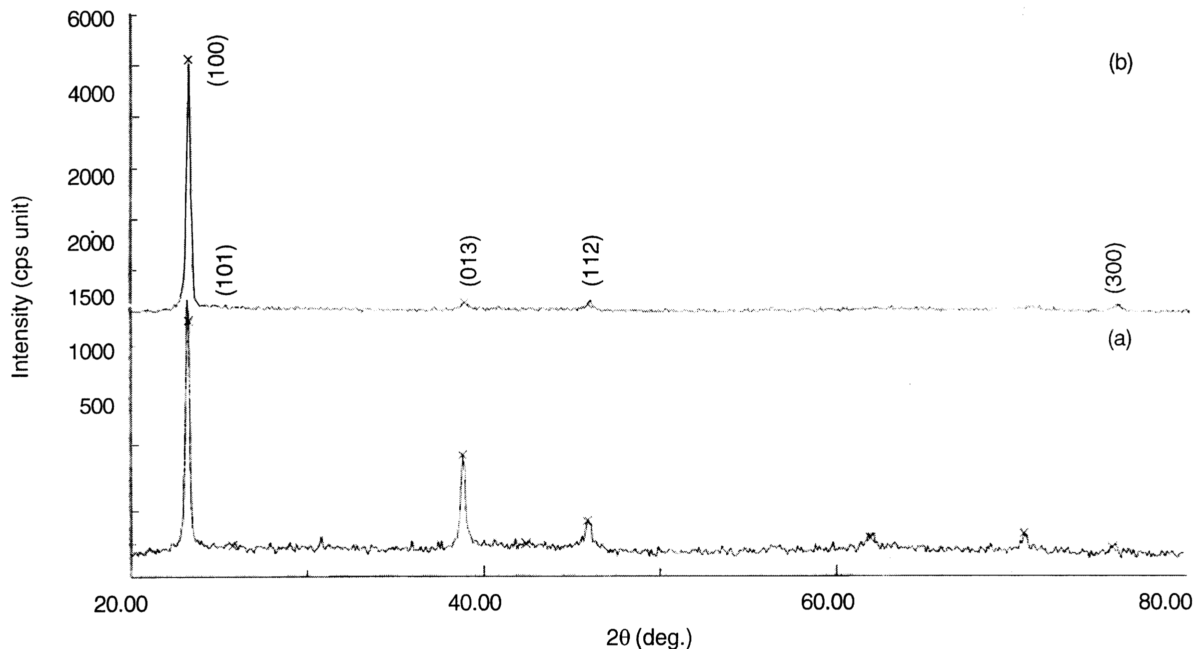

Fig. 7. X-ray diffractogram of CdTe thin films annealed at 573 K of (a) thickness 2000 Å and (b) thickness 2500 Å.

Table 2
Comparison of standard and observed XRD data

Standard						Observed		
2θ	*d*-value	Intensity	*h*	*k*	*l*	2θ	*d*-value	Intensity
23.920	3.721	70	1	0	0	23.300	3.8144	100
25.474	3.501	49	1	0	1	25.800	3.4502	13
35.693	3.485	13	0	1	3	38.800	2.3189	48
42.873	2.110	316	0	1	4	42.400	2.1300	13
45.812	1.980	70	1	1	2	45.900	1.9754	22
61.629	1.504	55	2	0	4	61.900	1.4977	15
70.457	1.337	69	1	1	6	70.700	1.3313	17
75.604	1.258	22	0	2	6	75.700	1.2553	12
76.881	1.240	10	3	0	0	76.000	1.2511	07

(1 0 0) plane of the standard data file (JCPDS 82-0474) indicating hexagonal structure having lattice parameters $a = 4.292$ Å and $c = 10.235$ Å and comparison of standard and observed data is presented in Table 2. From these diffraction patterns, it appears that the growth of films is of preferred orientation i. e. columnar growth perpendicular to substrate as indicated by low intensity of peaks observed in annealed samples. The low intensity peaks that appeared on annealing may be due to random orientation of grains. Diffraction analysis indicates that CdTe films are polycrystalline and grain sizes are determined by using Scherrer formula [31]:

$$C_s = \frac{K\lambda}{B\cos\theta} \tag{5}$$

where the constant K is a shape factor usually $\simeq 1$, λ the wavelength of the X-ray (1.5418 Å), θ the Bragg's angle and B is the corrected FWHM. The range of crystallite size estimated for as-deposited film sample (2000 Å thickness) is 63.82 Å while for annealed sample (2000 Å thickness) it was from 69.85 to 79.10 Å and that for 2500 Å thick annealed sample ranged from 69.85 to 95.75 Å, respectively. The effect of annealing and thickness as observed is that crystallite size increases and improves the structure of the film [29]. The crystallite size is by definition, measured in a direction normal to the reflection plane (1 0 0), i.e. in the ⟨1 0 0⟩ direction and consequently perpendicular to the substrate [10,30–32]. Therefore the observed increase in crystallite size may be interpreted in terms of a columnar grain growth. From the XRD analysis, it may be found that CdTe films have hexagonal structure having parameters estimated from computer program POWD (an Interpretation and Indexing Program, version 2.2) $a = 4.4045$ Å and $c = 10.235$ Å

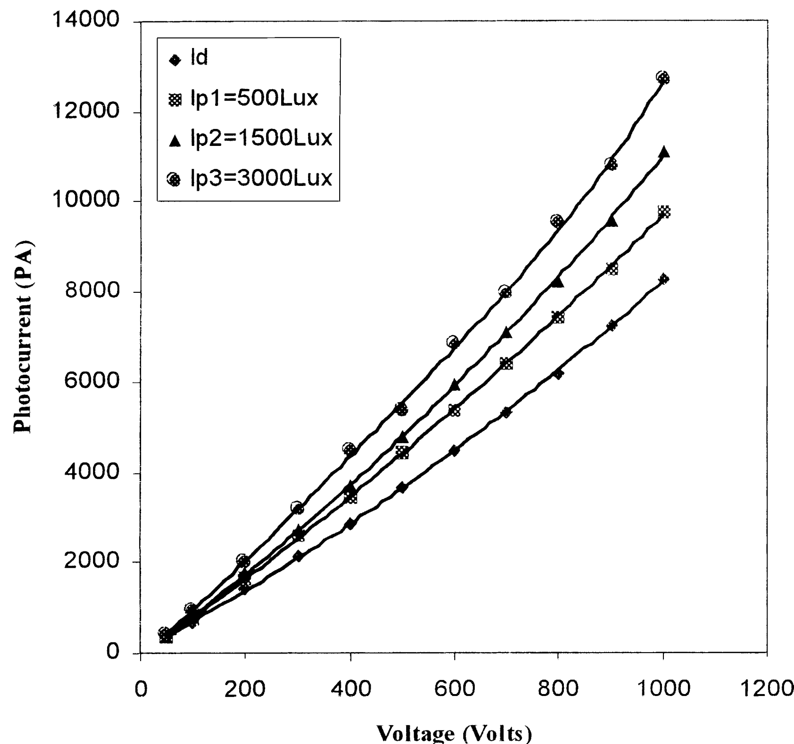

Fig. 8. Variation of photocurrent vs. voltage for CdTe ($d = 3000$ Å) thin film.

which are in good agreement with the standard (JCPDS 82-0474).

CdTe films deposited by PVD methods at different substrate temperatures have mixed structure of cubic and hexagonal [20]. However El-Kadary et al. [31], and Rusu and Rusu [32] have reported that thermally evaporated films have cubic structures.

An attempt is made to study photoconductive characteristic of the sample of thickness 3000 Å and the *I–V* characteristic is presented in the Fig. 8. It is observed that the CdTe films are of low photosensitivity. For low accelerating voltage up to 500 V photosensitivity is very low, while it increases at high accelerating voltages above 600 V. Maximum photosensitivity for largest excitation intensity 3000 lx is around 1.5–1.6.

4. Conclusions

Single-phase polycrystalline CdTe films have been deposited onto amorphous glass substrates as revealed from XRD analysis and evaluated crystallite size ranging from 63 to 95 Å only. Annealing of the samples improve crystallinity of the films. The dependence of the optical parameters of the films on the light energy supports the direct character of the interband transition through an optical band gap in the range 1.45–1.50 eV. The variation in optical constants as a function of wavelength is oscillatory in nature, which depends on the thickness of the sample. CdTe films are of low photosensitivity.

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References

[1] B.B. Ismaiel, R.D. Gold, Phys. Status Solidi A 115 (1989) 237.
[2] K.L. Chopra, S.R. Das, Thin Film Solar Cells, Plenum Press, New York, 1983.
[3] M. Takahashi, K. Uosaki, H. Kita, J. Appl. Phys. 55 (1984) 3879.
[4] F. Wang, D.K. Reinhard, J. Appl. Phys. 55 (1984) 3702.
[5] T.C. Anthony, A.L. Fahrenbruch, R.H. Bube, J. Vac. Sci Technol. A 2 (1984) 1296.
[6] B.J. Feldman, J.L. Boone, T.V. Van Doren, Appl. Phys. Lett. 38 (1981) 703.
[7] N. Matsumura, T. Ohshima, J. Saraie, Y. Yodogawa, J. Cryst. Growth 71 (1985) 361.
[8] H. Matsumoto, K. Kuribayashi, H. Uda, Y. Kamatsu, A. Nakano, S. Ikegami, Sol. Cells 11 (1984) 367.
[9] S. Gongoi, K. Barua, Thin Solid Films 92 (1982) 227.
[10] A. Ashour, M.R. Ebid, N. El-Kadry, M.F. Ahmed, A.A. Ramadan, Appl. Surf. Sci. 89 (1995) 159.
[11] N. El-Kadry, A. Ashour, M.F. Ahmed, K. Abdel-Hady, Thin Solid Films 259 (1995) 194.
[12] A.A. El-Shazly, H.T. El-Shair, Thin Solid Films 78 (1981) 287.
[13] A.A. El-Shazly, H.T. El-Shair, M.K. El-Mously, Thin Solid Films 78 (1981) 295.
[14] J. Aranda, J.L. Morenza, J. Esteve, J.M. Codina, Thin Solid Films 120 (1984) 23.
[15] G.K.M. Thutupalli, S.G. Tomlin, J. Phys. D 9 (1976) 1639.
[16] D. Poleman, J. Vennik, J. Phys. D 21 (1988) 1004.
[17] M. Melendez-Lira, S. Jimenez-Sandoval, I. Hernandez Calderson, J. Vac. Sci. Technol. A 7 (1989) 1428.
[18] J.J. Pankove, Optical Processes in Semiconductors, Prentice-Hall, Englewood Cliffs, NJ, 1971.
[19] A. Goswami, Thin Film Fundamentals, New Age International Pvt. Ltd., (1996) pp. 442.
[20] T.H. Myers, S.W. Edwards, J.F. Schetzina, J. Appl. Phys. 52 (1981) 4231.
[21] J.C. Manifacier, M. De Murcia, J.P. Fillard, E. Vacario, Thin Solid Films 41 (1977) 127.
[22] D.T. Marple, J. Appl. Phys. 35 (1964) 539.
[23] M. Cardona, K.L. Shaklee, F.H. Pallak, Phys. Rev. 154 (1967) 696.
[24] S. Chaudhari, S.K. Das, A.K. Pal, Thin Solid Films 147 (1987) 9.
[25] N. El-Kadry, M.F. Ahmed, K. Abdel Hady, Thin Solid Films 274 (1996) 120.
[26] B.A. Tavger, F.Ya. Demikhovskii, Sov. Phys. Usp. 11 (1968) 644.
[27] F. Cerdeira, I.T. Torriani, P. Mostisuke, V. Lemos, F. Decker, Appl. Phys. A 46 (1988) 107.
[28] R.F.C. Farrow, G.R. Jones, G.M. Williams, I.M. Young, Appl. Phys. Lett. 39 (1981) 954.
[29] A. Ashour, J. Mater. Sci.-Mater. Electron. 5 (1994) 47.
[30] A.H. Eid, S. Mahmoud, M.M. Sayed, Fizika 4 (1987) 397.
[31] N. El-Kadry, A. Ashour, S.A. Mahmoud, Thin Solid Films 269 (1995) 112.
[32] G.G. Rusu, M. Rusu, Solid State Commun. 116 (2000) 363.