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X-ray, electron microscopy and photovoltaic studies on CdTe thin films deposited normally at different substrate temperatures

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X-ray diffraction, transmission electron microscopy and electron diffraction studies were conducted on CdTe thin films deposited on glass substrates kept at different substrate temperatures. Variation of the different structural parameters, such as lattice constant, crystallite size, r.m.s. strain, dislocation density and stacking fault probability with substrate temperature, was investigated in the temperature range 300 to 498 K. An increase in the lattice constant and crystallite size values and a decrease in the other parameters with increase in temperature of the substrate was observed. A photovoltage was observed for CdTe film deposited normally on glass substrates kept at higher substrate temperatures. The development of photovoltage in the film is explained in the light of the formation of crystallites of variable structure.

1. Introduction

Studies on cadmium telluride films have already attracted wide attention because of their importance as good photovoltaic material. The dependence of high-voltage photo e.m.f. on structural properties has been reported by Semiletov [1] and Pensak [2]. Saha *et al.* [3] reported the variation of crystallite size, microstrain, dislocation density and stacking fault probability with various thicknesses of CdTe films deposited at room temperature. An investigation of the structure of CdTe film vacuum-deposited at high substrate temperatures was carried out by Shiojiri *et al.* [4]. However, these works deal with a qualitative observation of the defects and grain sizes from electron microscopy. Unlike lead and tin chalcogenides, no quantitative determination of the different microstructural parameters, such as crystallite size, r.m.s. strain, dislocation density, stacking faults probability etc. have been reported for cadmium telluride. Hence X-ray line profile analysis and electron microscopy studies of the structural parameters at various substrate temperature (300 to 498 K) were undertaken in the present work.

Semiltov [1] and Johnson *et al.* [5] reported the anomalous photovoltaic effect only for films in which the molecular beam impinged the substrate at a large angle of incidence. No photovoltaic effect was observed in the case of normal deposition of CdTe films. A photovoltaic effect was also in films deposited normally on the substrate. The magnitude of the observed photo e.m.f. in normal deposition is small compared with the reported value for films of oblique deposition.

2. Experimental procedure

Thin films were prepared from polycrystalline powder of CdTe which was obtained through direct synthesis of cadmium (99.999%) and tellurium (99.999%) in an evacuated (10^{-4} Pa) graphite-coated quartz tube. The final compound was confirmed to be CdTe with fcc structure using X-ray analysis. The lattice parameter was found to be quite close to the reported value.

Prior to deposition, the substrates were cleaned with warm chromic acid and distilled water. Thin films were deposited by evaporating CdTe powder from a quartz crucible placed in a tungsten coil in a vacuum of the order of 10^{-4} Pa on glass substrates, with the help of a Hind Hivac Vacuum Coating unit (Model 12-A4). The rate of deposition was maintained constant at 3.5 nm sec^{-1}. The thickness of the films was measured using surphometer (SF 101). During the deposition of the films at various substrate temperatures (300 to 498 K) the thicknesses of the films remained almost constant. It was observed that films were not well deposited on the substrate at substrate temperatures higher than 498 K. Hence the maximum substrate temperature used did not exceed 498 K. X-ray diffraction data were recorded with the help of a Philips X-ray diffractometer using Mo$K\alpha$ radiation.

The diffracted intensities from the films were found to be polycrystalline type and the line profiles were subjected to variance analysis for calculating the crystalline size and microstrain. Because the method is sensitive to the variation of X-ray intensity near the tails, the peaks were carefully corrected for background radiation by the method given by Mitra and Mishra [6]. As the variances were additive the profiles were corrected for instrumental broadening by subtracting the variance of the corresponding profile for standard well-annealed CdTe samples. Assuming the broadening of the X-ray line to be due to crystallite

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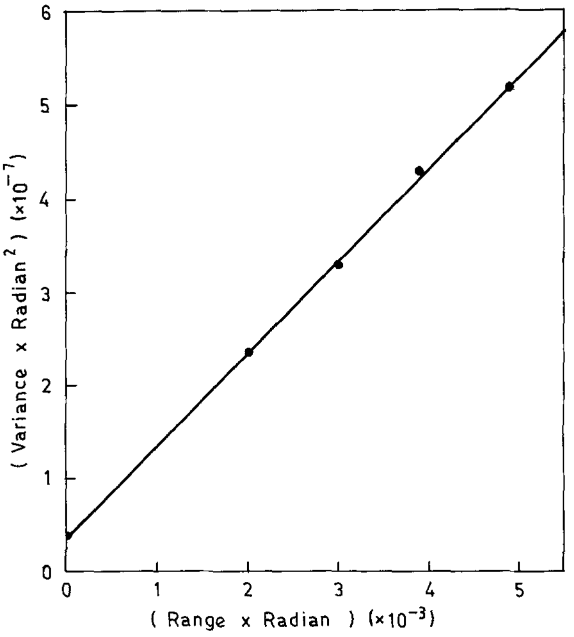

Figure 1 Plot of variance (W) against range (σ) for films deposited at 498 K substrate temperature.

size and strain only, the variance can be given by

$$W_{2\theta} = \frac{\lambda\sigma}{2\pi^2 P\cos\theta} + 4\tan^2\theta\langle e^2\rangle$$

where σ is the angular range, P the crystallite size, $\langle e^2\rangle$ the mean squared strain, λ the wavelength of the X-rays and θ the Bragg angle. A plot of $W_{2\theta}$ against σ is a straight line whose slope gives the crystallite size and the intercept gives the strain. Dislocation densities were calculated from P and $\langle e^2\rangle$ using the method of Williamson and Smallman [7]. The stacking fault probabilities were estimated from the peak shift of the X-ray lines with reference to that from well-annealed samples, using the method given by Warren and Warekois [8].

The lattice parameters for different films were calculated from the Nelson and Riley [9] plots. The variance (W)–range (σ) plot for a typical film of 700 nm thickness deposited at 498 K substrate temperature, is shown in Fig. 1. The linearity of the plots shows that the background has been adjusted properly.

Transmission electron microscopy (TEM) as well as transmission electron diffraction patterns were obtained with the help of a Jeol, JEM 200 CX electron microscope. The electron micrographs as well as the electron diffraction patterns of the films deposited at different substrate temperatures are shown in Fig. 2.

The composition of the films deposited at various substrate temperatures were estimated using EDX (Camscan Series II) study.

The films deposited in vacuum and exposed to the atmosphere after deposition are found to be p-type as determined by thermoelectric measurements. A tungsten filament lamp fed by a regulated power supply was used as the source of light and the intensity of the light falling on the sample was determined with the help of an Eppley thermopile. The intensity of the light falling on the sample was 3000 W m^{-2} in all cases.

Photovoltages were measured with a high-impedance ($10^{14}\ \Omega$) electrometer amplifier (EC 046) on films deposited at different substrate temperatures keeping

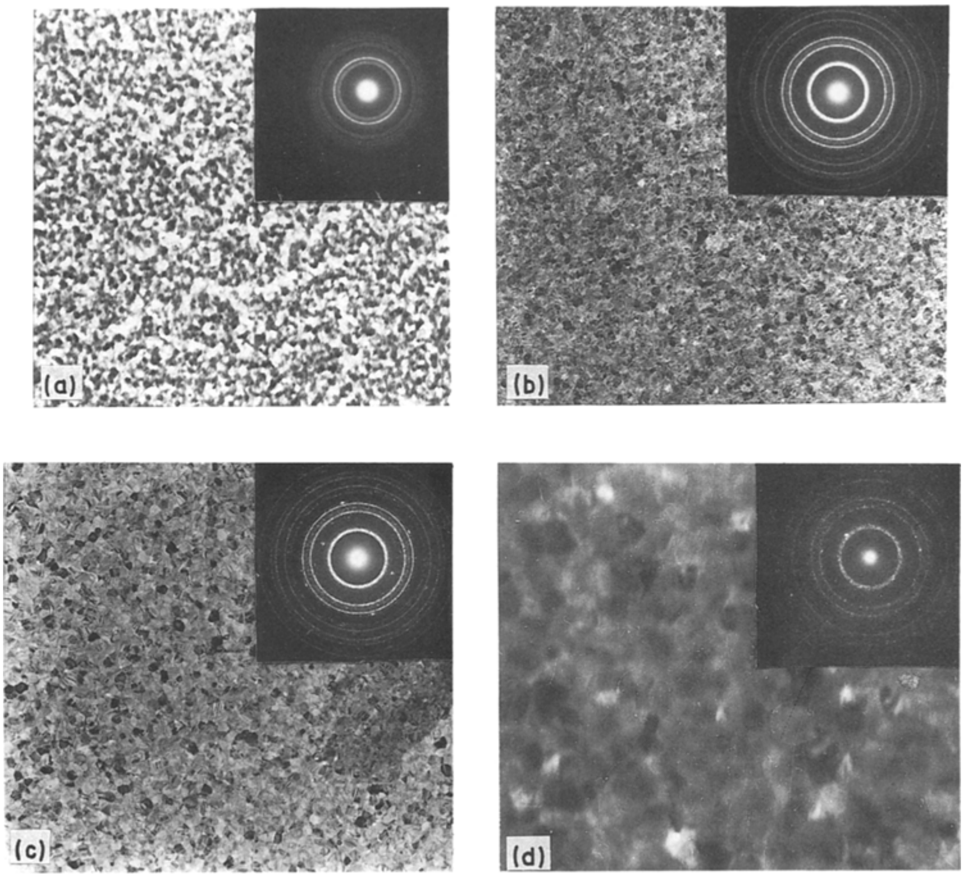

Figure 2 Electron micrographs and electron diffraction of films deposited at different substrate temperatures. (a) 300, (b) 363, (c) 423 and (d) 498 K. ×60 000.

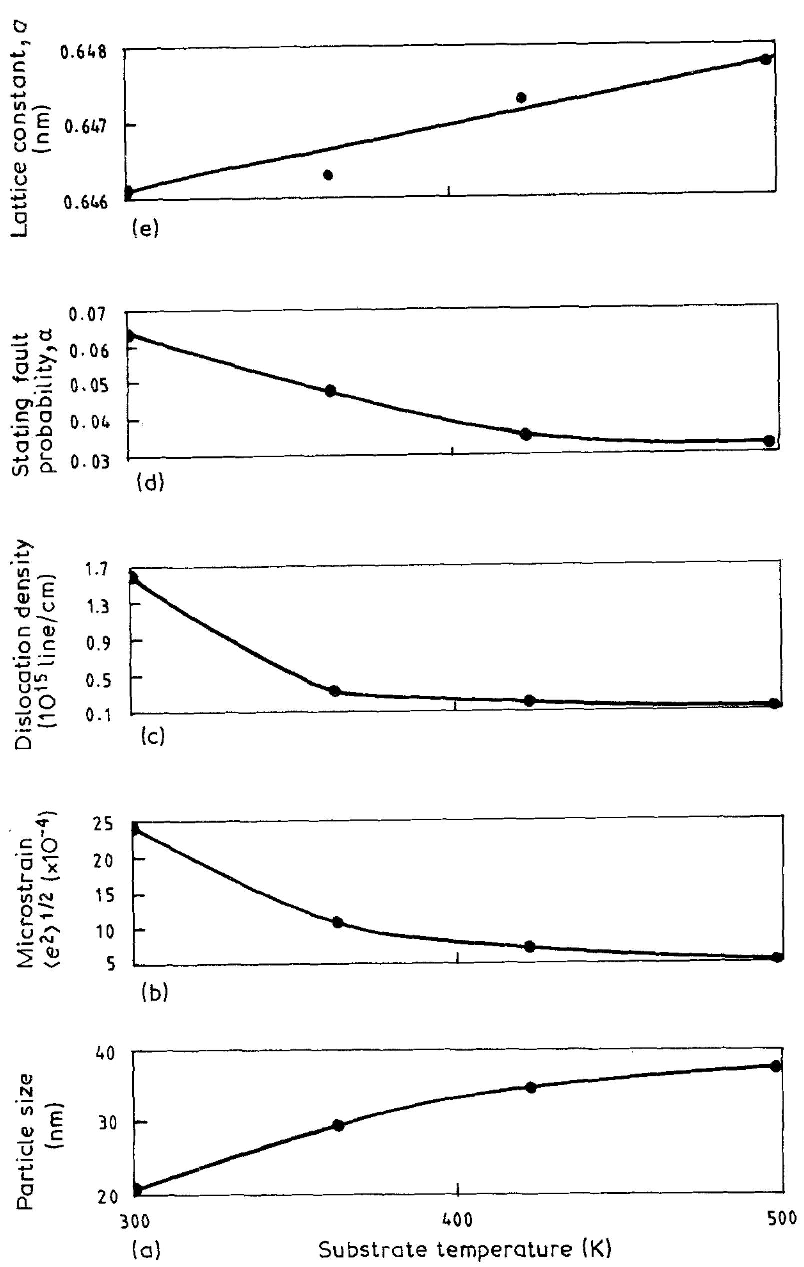

Figure 3 Plots of substrate temperature against (a) particle size, (b) microstrain, (c) dislocation density, (d) stacking fault probability and (e) lattice constant.

the thickness of the film constant. Photovoltages were also measured for films of different thickness keeping the substrate at the highest possible temperature, i.e. 498 K.

3. Results and discussion

The X-ray and electron diffraction patterns show that the films deposited at room temperature have face-centred cubic structure with $a = 0.6461$ nm. It is also observed from the X-ray diffraction patterns that the crystallites are preferentially oriented with the (1 1 1) face parallel to the substrate. The values of the particle size, r.m.s. strain $\langle e^2 \rangle^{1/2}$, dislocation density ($\rho$), stacking fault probability (α), lattice constant (a) are given in Table I. Plots showing the variation of these parameters with substrate temperature are shown in Fig. 3. Values of the interplanar spacings obtained from the electron diffraction patterns are given in Table II.

It was observed that with increasing substrate temperature there was a gradual increase in the lattice constant which tended towards the bulk value and had a value of 0.6477 nm for films deposited at 498 K. With further increase in substrate temperature there was a gradual increase in the crystallite size and a gradual decrease in the r.m.s. strain, dislocation density and stacking fault probability.

The rate of decrease was sharper initially and much

TABLE I Microstructural parameters for vacuum-deposited CdTe thin films at different substrate temperature

Thickness (nm)	Substrate temperature (K)	Particle size, P (nm)	Microstrain $\langle e^2 \rangle^{1/2}$ ($\times 10^{-4}$)	Dislocation density, ρ (10^{15} line/m^2)	Stacking fault probability, α	Lattice constant, a (nm)	Te/Cd (at %)
700	300	22.0	24	1.62	0.063	0.6461	1.273
710	363	29.7	10.70	0.34	0.048	0.6463	1.254
705	423	34.7	7.1	0.19	0.035	0.6473	1.145
700	498	37.9	5.0	0.12	0.032	0.6477	1.114

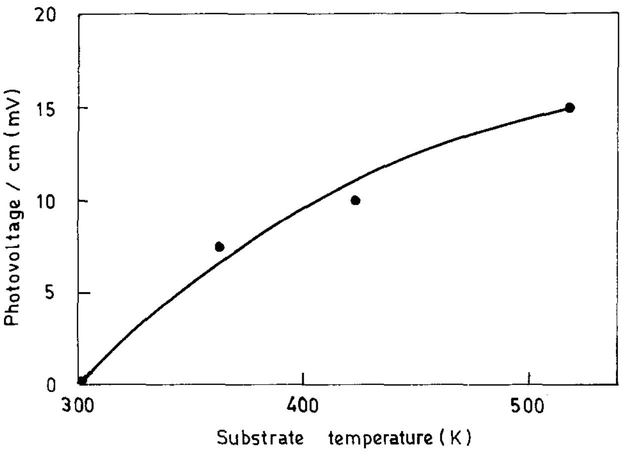

Figure 4 Plot of photovoltage per centimetre length of the film against substrate temperature.

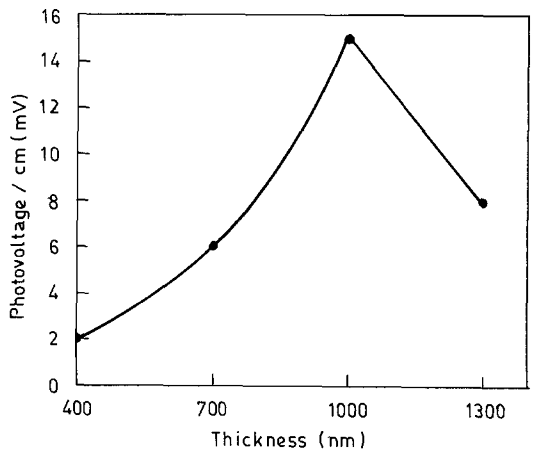

Figure 5 Plot of the inverse of the intensity against q^2 for samples aged for (⊙) 22 h, (▲) 50 h and (+) 135 h, at 475° C.

slower at higher substrate temperature. This is possibly due to the fact that with increasing substrate temperature greater re-evaporation and diffusion in the disordered regions leads to recrystallization. Because of this there is an increase in the size of the ordered regions leading to an increase in the crystallite size and decrease in other defect parameters. However, possibly at still higher substrate temperature a sort of equilibrium may be reached and hence there will be less appreciable change in the parameters.

An increase in the size of the crystallites with substrate temperature was also evident from the electron micrographs. With increasing temperature the electron diffraction lines become more and more sharp, indicating an increase in size. At low substrate temperatures the electron diffraction patterns also showed weak tellurium lines indicating the presence of traces of excess tellurium. However, at higher substrate temperatures these lines vanished. EDX measurements made on the films also confirmed the above observations. Films deposited at 423 K exhibited a few spots in the electron diffraction pattern, which corresponded to the hexagonal phase of CdTe. Similar observations were also reported by Pal *et al.* [10] for ZnTe films which have the same type of structure.

No photovoltage was observed in CdTe films deposited by normal incidence keeping the substrate at room temperature. But the films obtained at higher substrate temperatures showed a photovoltaic effect. The magnitude of the photovoltage was found to increase with increasing substrate temperature during deposition (Fig. 4, Table III). From the thickness variation of photovoltage, keeping the substrate at the highest possible temperature (498 K), it was seen (Fig. 5, Table IV) that the photovoltage increased to a thickness of 1 μm and it began to fall for thicker film. As already mentioned the film obtained at room temperature and those obtained at higher substrate temperatures differed in the number of stacking faults and the proportion of the two types of crystallites, cubic and hexagonal. Initially at room temperature the crystallites were almost cubic. The hexagonal phase became more and more prominent with increasing substrate temperature. Thus the photo-e.m.f. in such a CdTe film develops in the transition regions between the hexagonal and cubic packing. The potential barrier set up at an interface between the two structures due to a combination of the band gap difference [11] seems to be responsible for this photo-e.m.f. Therefore, together with the other parameters, the structure transition also contributes to some extent to the build up of anomalous photovoltage in CdTe films. The decrease in photovoltage of films of thickness greater than 1 μm may be due to a sudden increase of stacking fault probability [3] which in turn decreases the magnitude of the potential barrier.

TABLE II Interplanar spacings of the films deposited different substrate temperatures as measured from TED

Reflection	*d* values at			
	300 K	363 K	423 K	498 K
1 1 1	0.3742	0.3742	0.3742	0.3742
2 2 0	0.2335	0.2364	0.2364	0.2264
3 1 1	0.2055	0.2081	0.2024	0.1994
4 0 0	0.1706	0.1651	0.1642	0.1591
3 3 1	0.1535	0.1515	0.1555	0.1459

TABLE III Photovoltage of the films deposited at different substrate temperature

Thickness (nm)	Substrate temperature (K)	Photovoltage/cm (mV)
1000	300	0
1100	363	7.5
1000	423	10.0
1090	498	15.0

TABLE IV Photovoltage of the films deposited at different thickness

Substrate temperature (K)	Thickness (nm)	Photovoltage/cm (mV)
498	400	2
498	700	6
498	1000	15
498	1300	8

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