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X-Ray Line Broadening and Electron Microscopic Studies on ZnTe Thin Films

By

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X-ray diffraction, transmission electron microscopy, and transmission electron diffraction studies on zinc telluride thin films deposited on glass substrates are made. The variation is studied of different structural parameters like crystallite size, r.m.s. strain, dislocation density, and stacking fault probability with thickness of the films as well as with substrate temperature. Maximum crystallite size and minimum dislocation density are observed corresponding to a substrate temperature of 573 K. The hexagonal phase is observed along with the predominant cubic phase at substrate temperatures beyond 623 K.

Röntgenbeugungs-, Transmissionselektronenmikroskopie- und Transmissionselektronenbeugungsuntersuchungen an dünnen Zinktelluridschichten auf Glassubstraten werden durchgeführt und die Änderung verschiedener Strukturparameter wie Kristallitgröße, r.m.s-Spannung, Versetzungsdichte und Stapelfehlerwahrscheinlichkeit mit der Schichtdicke sowie der Substrattemperatur wird untersucht. Maximale Kristallitgröße und minimale Versetzungsdichte werden bei einer Substrattemperatur von 573 K beobachtet. Zusammen mit der dominierenden kubischen Phase wird bei Substrattemperaturen oberhalb 623 K die hexagonale Phase beobachtet.

1. Introduction

ZnTe is a semiconductor belonging to the $A^{II}B^{VI}$ group with a band gap of about 2.25 eV at 300 K and is of great importance because of its use in switching devices, solar cells, detectors, etc. Because of its importance several workers [1 to 7] have made a detailed study of the crystal structure of ZnTe thin films. They have observed that these films deposited on glass substrates kept at room temperature have cubic zincblende-type structure with one-dimensional stacking disorder. An increase in the stacking disorder resulting in the formation of hexagonal crystallites of wurtzite type has been observed in case of substrates kept at higher temperatures. Brown and Brodie [6] have also reported the formation of noncrystalline ZnTe thin films for low substrate temperatures. However, most of these works deal with a determination of the structure type and a qualitative observation of the defect and grain size from electron microscopy. No quantitative determination of the different microstructural parameters like the size of the crystallities, microstrain, dislocation density, stacking fault probability, etc. has been reported in case of ZnTe thin films. Hence in the present paper a determination of the above parameters has been undertaken for ZnTe thin films (400 to 1020 nm) using X-ray line profile analysis, transmission electron microscopy (TEM) and transmission electron diffraction (TED) techniques. Effect of substrate temperature on the growth of the films has also been studied.

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2. Experimental

The films were deposited by evaporating ZnTe powder from a quartz crucible placed in a tungsten coil in a vacuum of the order of 10^{-4} Pa on properly cleaned glass substrates with the help of a Hind Hivac vacuum coating unit (Model 12-A4). The rate of deposition was maintained at a constant rate of 2 nm/s. The thickness of the films was measured by surphometer (SF 101) as well as by interference methods.

The deposition of films at high substrate temperatures was carried out in a suitable apparatus described elsewhere [14].

The X-ray diffractographs were recorded with the help of a Norelco X-ray diffractometer at a scanning speed of 0.5°/min by using monochromatic MoK_α radiation. Transmission electron micrographs and transmission electron diffraction patterns were obtained with the help of a (JEOL, JEM 200 CX) electron microscope.

The intensities of the X-ray diffraction line profiles were subjected to variance analysis [8] for calculating the crystallite size and microstrain. Since the method is sensitive to the variation near the tails of the peaks, a careful adjustment of the background was carried out following the method of Mitra and Misra [9]. The profiles were corrected for the instrumental broadening by subtracting the variances of the corresponding profiles of well annealed ZnTe samples. Assuming the broadening of the line to be due to crystallite 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. Dislocation densities have been calculated from the particle size and r.m.s. strain values by using the relations given by Williamson and Smallman [10].

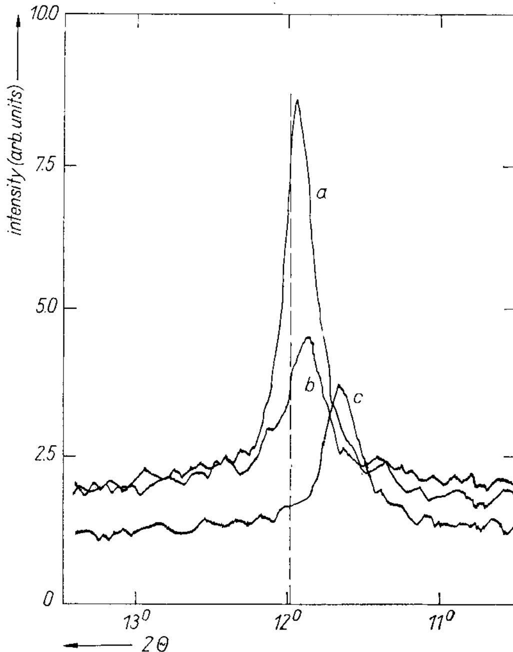

Fig. 1. X-ray diffraction profile of (a) 1020 nm, (b) 630 nm, (c) 270 nm films showing peak shift and line broadening. The vertical line is showing the position of the well annealed powdered sample

The f.c.c. crystals are formed by a stacking of the densely packed (111) planes in the proper sequence ABCABC ... A deviation in the sequence gives rise to the h.c.p. stacking of ABAB type and is known as stacking fault. The stacking fault probability α is the fraction of layers undergoing stacking sequence faults in a given crystal and hence one fault is expected to be found in $1/\alpha$ layers. Occurrence of stacking faults gives rise to a shift in the peak positions of different reflections with respect to the

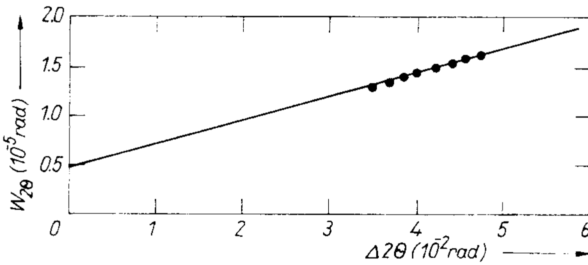

Fig. 2. Variance vs. range for 650 nm film deposited at 573 K substrate temperature

ideal positions of a fault-free, well annealed sample. Three typical experimental profiles, showing the peak shift for (111) reflection of films of different thickness with respect to a well annealed bulk sample are shown in Fig. 1. Warren and Warekois [11] have given a relation connecting α with the peak shift $\Delta(2\theta)$. The stacking fault probability α is given by

$$\alpha = \frac{2\pi^2}{45\sqrt{3}\tan\theta_{111}}\,\Delta(2\theta^0)\,.$$

In the present case the fault probabilities have been calculated from the shift of the peaks of the X-ray lines of the films with reference to that from a well annealed sample by using the above expression. The variance (W) versus range (σ) plot for a typical film of 650 nm thickness deposited at 573 K substrate temperature is shown in Fig. 2. The linearity of the plot shows that the background has been adjusted properly.

3. Results and Discussion

The X-ray and electron diffraction patterns show that the films deposited on the substrates kept at room temperature have face-centred cubic structure with $a = 0.610$ nm. It is also observed from the X-ray diffraction patterns that the crystallites are preferentially oriented with (111) face parallel to the substrate. The values of the particle size, microstrain, dislocation density and stacking fault probability for films of different thickness are given in Table 1. Corresponding values for films deposited at different substrate temperatures are compiled in Table 2. The variation of the crystallite size and r.m.s. strain with thickness of the films is shown in Fig. 3 and the variation of dislocation density and stacking fault probability with thickness is shown in Fig. 4. The variation of the different microstructural parameters with substrate temperature can be taken from Fig. 5 and 6.

Table 1

Microstructural parameters for ZnTe films of different thickness deposited at room temperature in vacuum

film thickness (nm)	crystallite size p (nm)	r.m.s. strain $10^4\langle e^2\rangle^{1/2}$	dislocation density ϱ (10^{15} lines/m^2)	stacking fault probability α
400	6.0	304	49.5	0.351
630	6.8	225	33.8	0.073
700	7.2	231	32.8	0.067
800	8.0	250	36.9	0.067
1020	9.7	291	30.5	0.024

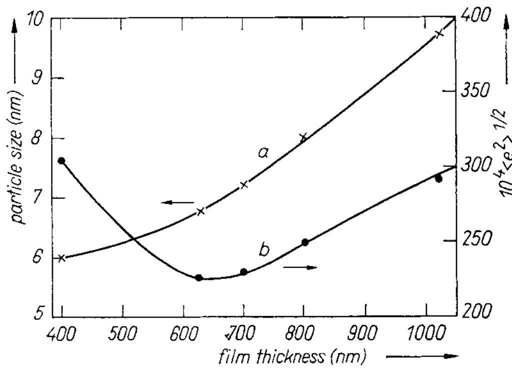

Fig. 3. (a) Particle size and (b) micorstrain vs. film thickness for the films deposited at room temperature

Table 2

Microstructural parameters for ZnTe films deposited at different substrate temperatures in vacuum

substrate temperature T_s (K)	film thickness (nm)	crystallite size p (nm)	r.m.s. strain $10^4\langle e^2\rangle^{1/2}$	dislocation density ϱ (10^{15} lines/m^2)	stacking fault probability α
305	630	6.8	225	33.8	0.073
373	550	7.5	99	13.0	0.109
473	600	8.0	61	7.9	0.079
573	650	15.0	105	7.1	0.085
673	600	4.2	80	19.4	0.266

It is observed that the crystallite size values as well as the microstrain values gradually increase with increase in the film thickness. The dislocation density value slowly decreases with increase in the thickness of the films. It is also observed that the stacking fault value is very high for thinner films and decreases with increase in thickness.

As had been mentioned earlier ZnTe has zinc sulphide structure and can give close-packed cubic or close-packed hexagonal structure. Since there is very little energy difference between the two structures, sometimes both structures are observed simultaneously. The only difference in the zincblende-type (cubic) and the wurtzite-

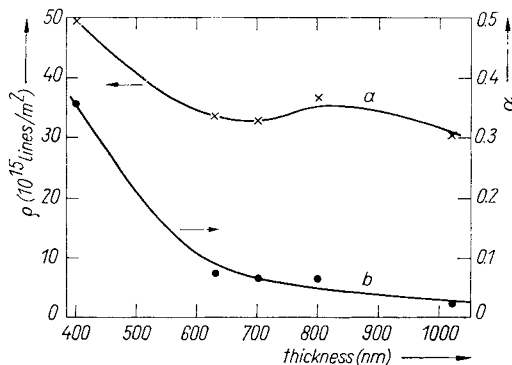

Fig. 4. (a) Dislocation density and (b) stacking fault probability vs. film thickness for films deposited at room temperature

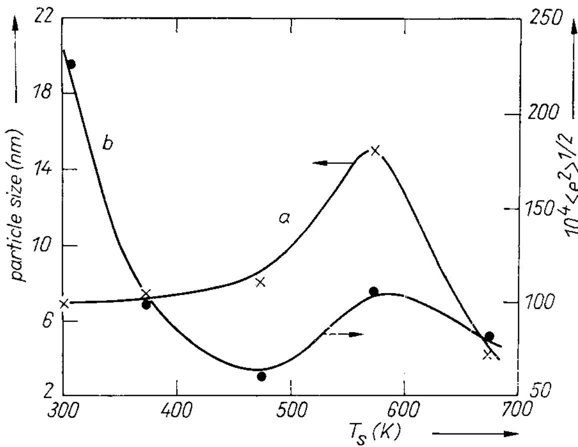

Fig. 5. (a) Particle size and (b) microstrain vs. substrate temperature of ZnTe films (≈ 600 nm)

type (hexagonal) structures is in the stacking sequence of the close-packed layers of atoms. There is very little energy difference between the two types and faults in one type give rise to the other type in the region of the fault. The stacking fault probability α is the fraction of layers undergoing fault in the stacking sequence and $1/\alpha$ gives the number of layers after which a fault occurs. In the present case large values of α are observed for very thin films. With increase in the thickness it decreases initially, but it again increases slightly for very thick films.

The transmission electron micrographs and corresponding electron diffraction patterns are shown in Fig. 7. Values of the interplanar spacings obtained from the electron diffraction patterns are tabulated in Table 3. The indices of the different cubic reflections are given in Table 3 and those for the hexagonal phase are shown within brackets.

An increase in the size of the particles with temperature is evident from the electron micrographs. Formation of the hexagonal phase at higher temperatures and microtwinning is observed from the contrast in the micrographs (lamellas within the grains). Similar observations are also made from the broadening of the X-ray and electron diffraction lines. It is observed that with increase in the temperature of the substrates the diffraction lines become more and more sharp thus indicating an increase in the size of the crystallites. Films deposited at about 573 K show maximum crystallite size. The X-ray line profile analysis study also shows that the crystallite size value increases

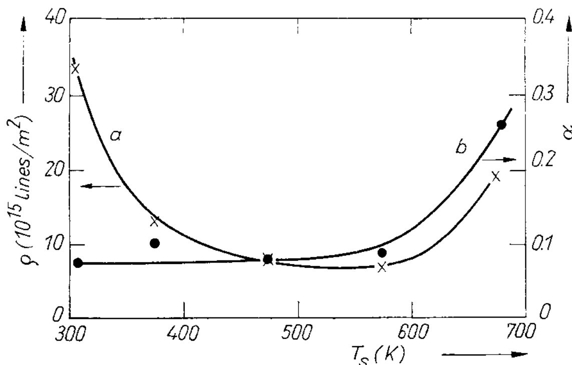

Fig. 6. (a) Dsilocation density and (b) stacking fault probability vs. substrate temperature of ZnTe films (≈ 600 nm)

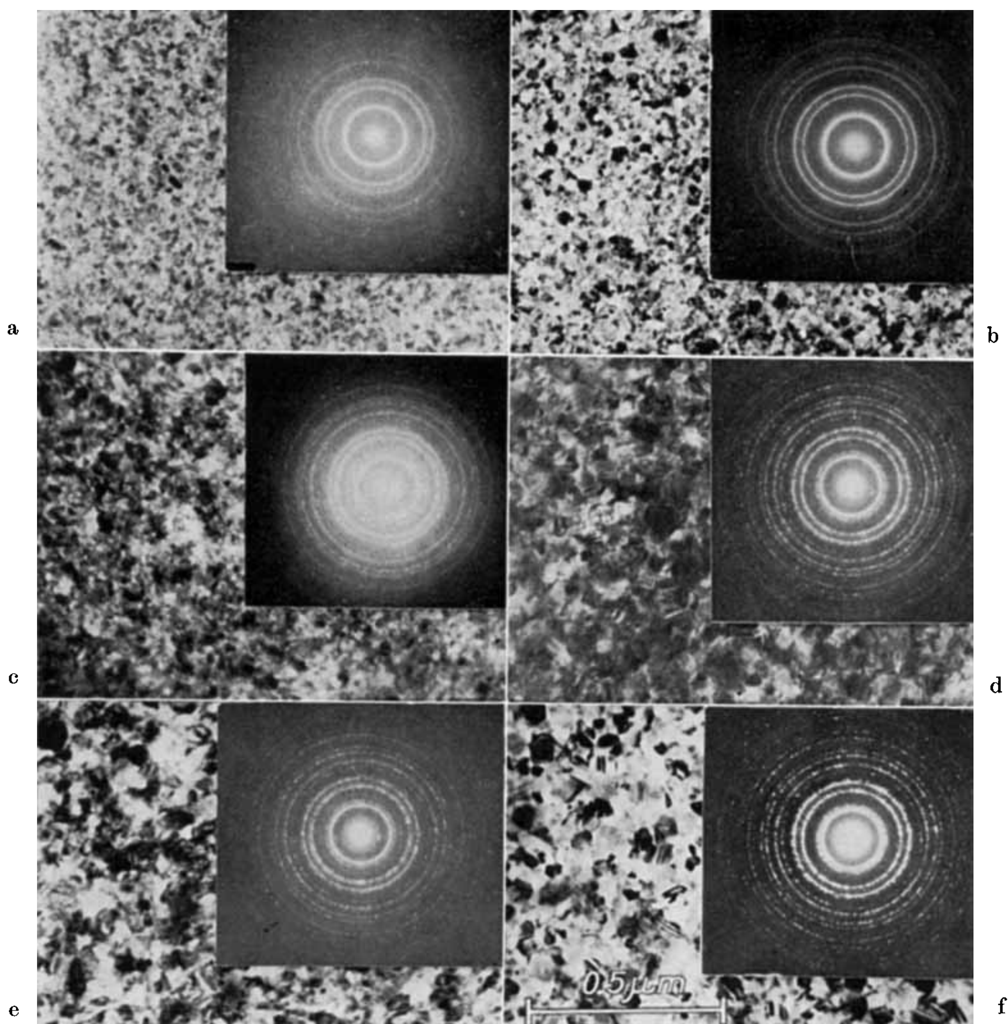

Fig. 7. TEM and TED photographs for films deposited at substrate temperatures a) 305 K (RT) (60 nm), b) 428 K (58 nm), c) 523 K (60 nm), d) 573 K (61 nm), e) 623 K (58 nm), and f) 723 K (57 nm)

with rising substrate temperature. The size value is maximum at 573 K and it decreases with further increase in the substrate temperature. The dislocation density is also observed to be minimum at the above temperature. With increase in the substrate temperature an increase in the stacking fault probability value is observed. Faint lines corresponding to the hexagonal phase are observed in case of films deposited at 623 and 723 K. Other workers [1 to 3] have also reported the development of the hexagonal phase at high substrate temperatures.

Okamoto [12] had, from optimal absorption studies, reported that the optimum substrate temperature for ZnTe films is 653 K, i.e. 0.38 of the boiling point of ZnTe. Patel and Patel [4] have observed from electrical resistivity measurements that the

Table 3

Interplanar spacings and corresponding indices (as observed from TED) for ZnTe films deposited at different substrate temperature

T_s = 305 K (RT)		T_s = 428 K		T_s = 523 K		T_s = 573 K		T_s = 623 K		T_s = 723 K	
interplanar spacing d (nm)	indices hkl	interplanar spacing d (nm)	indices hkl	interplanar spacing d (nm)	indices hkl	interplanar spacing d (nm)	indices hkl	interplanar spacing d (nm)	indices hkl	interplanar spacing d (nm)	indices hkl
0.353	111	0.352	111	0.351	111	0.352	111	0.352	111	0.353	111
0.215	220	0.215	220	0.252	$(10\bar{1}2)$	0.305	200	0.305	200	0.305	200
0.184	311	0.185	311	0.215	220	0.216	220	0.256	$(10\bar{1}2)$	0.214	220 $(11\bar{2}0)$
0.140	331	0.152	400	0.185	311	0.184	311	0.215	220 $(11\bar{2}0)$	0.198	$(10\bar{1}3)$
0.124	422	0.140	331	0.152	400	0.176	222	0.184	311	0.184	311
0.103	531	0.125	422	0.140	331	0.153	400	0.177	222 $(20\bar{2}1)$	0.175	222 (0004)
		0.118	511	0.124	422	0.140	331	0.153	400	0.150	400 $(20\bar{2}3)$
		0.103	531	0.118	511	0.124	422	0.140	331	0.140	331
				0.104	531	0.117	511	0.125	422	0.123	422 $(21\bar{3}3)$
						0.103	531	0.117	511	0.116	511 $(30\bar{3}2)$
						0.097	620	0.103	531	0.108	$(22\bar{4}0)$
						0.093	533	0.096	620	0.103	531
						0.085	711	0.095	533 $(13\bar{4}3)$	0.097	620
						0.082	642	0.086	711	0.085	711
						0.079	731	0.081	642	0.080	731
								0.079	731		

optimum temperature is 573 K, i.e. 0.33 of the boiling point. As mentioned earlier, in the present investigation it is observed from X-ray diffraction, TEM, and TED studies that the crystallite size is maximum and dislocation density is minimum at the substrate temperature of 573 K, i.e. 0.33 of the boiling point. Hence we can conclude that the optimum growth conditions for the films are at about one third the boiling point of ZnTe. This is in accordance with the theory of Vincett et al. [13] where the above criterion was obtained from thermodynamic considerations. At this temperature the reevaporation rate of the disordered region becomes equal to the deposition rate and there is substantial diffusion and recrystallisation in the films. They have verified the above criterion for many films and have concluded that sharply optimised properties are observed at substrate temperatures equal to one third of the boiling point of the substance. Santhanam et al. [14] have also observed a maximum crystallite size value for SnTe films at the optimum substrate temperature.

4. Conclusions

The microstructural parameters for the ZnTe thin films deposited on glass substrates were found to be critically dependent on the thickness and the substrate temperature of the films. Increase in the crystallite size and r.m.s. strain, decrease in dislocation density and stacking fault values are observed with increasing thickness of the films. With increase in the substrate temperature there is an increase in the crystallite size value and decrease in the dislocation density. The optimum values are obtained at a substrate temperature of 573 K which is about 0.33 of the boiling point of ZnTe. Further hexagonal phase of ZnTe is observed in films deposited at substrate temperatures higher than 623 K.

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