Structural characterization of ZnTe films by X-ray diffraction technique

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Abstract : Structural defects originating from the lattice misfit in ZnTe thin films can be minimized by depositing the films at elevated substrate temperatures (T_s) in the range 473K–623K and thereby enhancing the film crystallinity. The average stress and microstrain decrease in this T_s range. The conductivity is found to be maximum for film deposited at 473 K. These structural effects in correlation with film conductivity is expected to be governed by the predominant recrystallization process which facilates in reducing native defects in ZnTe films.

1. Introduction

Zinc telluride belonging to the II-VI group is one of the promising materials. The deposition of good quality ZnTe films has become increasingly important due to their large scale industrial applications. In thin films, point defects, microscopic or macroscopic disorders and boundary defects are much more numerous and complex than those present in crystalline bulk solid. This is because of their simultaneous interaction with one another in addition to their dependence on the growth process. In thermally evaporated films, the photoresponse and the structural characteristics are greatly influenced by the sensitive deposition parameters like the vacuum, the rate of deposition, substrate temperature and film thickness [1]. Thus, the study of the structural features of ZnTe films is also of great interest both from the scientific as well as from the application point of view. In the present work a brief quantitative assessment of some structural parameters as well as the conductivity in correlation with substrate temperature of thermally evaporated ZnTe films, have been reported.

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2. Experimental

Thin films of ZnTe were deposited on highly cleaned glass substrates held at different temperatures by usual thermal evaporation technique (HINDHIVAC 12A4). Specpure (99.999%) bulk ZnTe powder obtained from Koch Light Lab UK was used for deposition. A vacuum of the order of 10⁻⁶ torr, rate of deposition 4.5 Å/sec and the source to substrate distance at 6 cm were carefully maintained during preparation of all ZnTe films. A copper-constantan thermocouple in conjunction with a digital d.c. microvoltmeter was used to measure the substrate temperature (T_s). Film thickness (t) was measured by using the multiple beam interferometry method with an accuracy of ±20 Å. The conductivity of films was measured with the help of a high impedance ($\sim 10^{14}$ Ω) electrometer (ECIL) amplifier. The XRD patterns of ZnTe thim films were recorded with the help of a Philips X-ray diffractometer (PW1830) using CuKα radiations. The tube was operated at 30 KV, 20 mA with the scanning speed of 0.03° (2θ)/sec.

3.   Results and discussion

XRD patterns of ZnTe films having thickness 1300 Å deposited at T_s from 303 K to 623 K are shown in Figure 1. The as-grown thin films of ZnTe are found to be

Figure 1. (a)XRD Traces of ZnTe films (1300 Å) deposited at 303 K–623K and (b) for another film having thickness 2600 Å.

polycrystalline having fcc zincblende type structure irrespective of substrate temperature and thickness. All ZnTe films show an intense peak corresponding to [111] plane whose intensity increases with T_s. Another two prominent peaks due to [220] and [311] reflections appear for the ZnTe films deposited at above 423 K. This is confirmed from the standard JCPDS X-ray powder file data (card no. 15-746). Similar results are also reported by other workers [2,3]. The intensities [220] and [311] peaks are smaller than the [111] peak which indicate that the preferential orientation of the microcrystallites is along [111] direction, perpendicular to the substrate.

The lattice constant for each plane appeared in the XRD patterns is calculated for cubic phase structure. The corrected values of lattice constants are estimated from the Nelson-Riley plots (Figure 2) to eliminate systematic errors
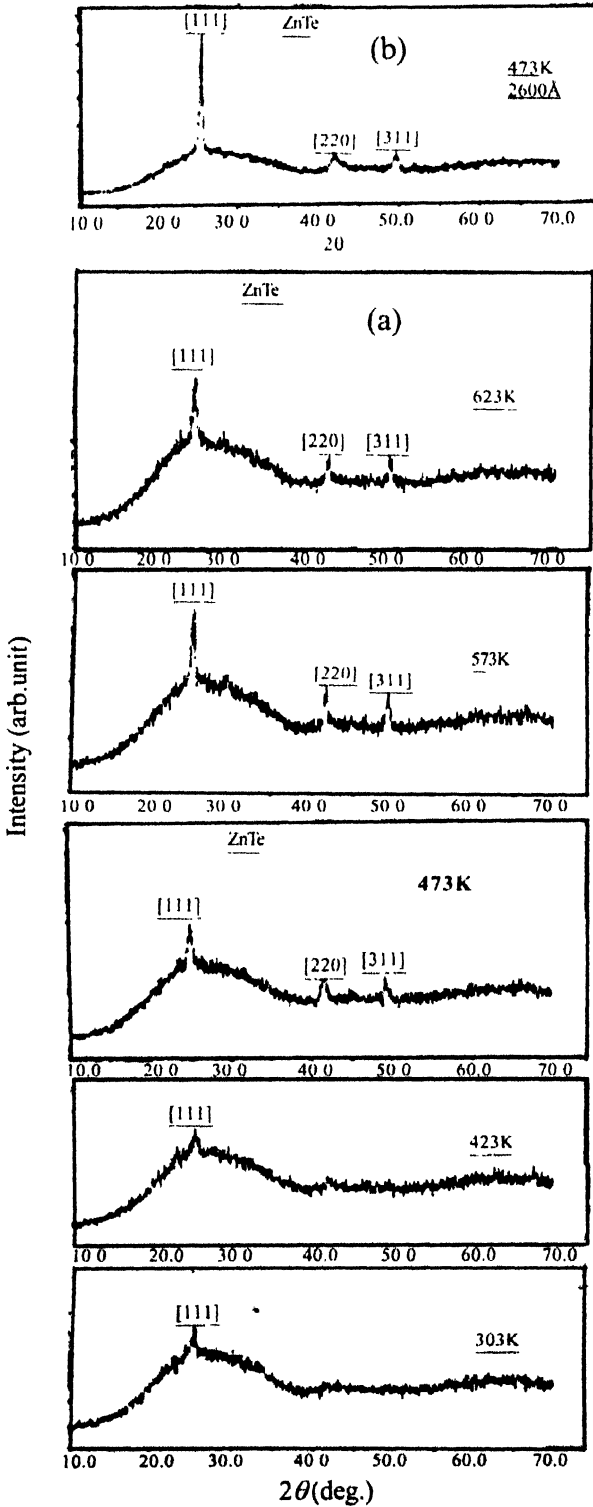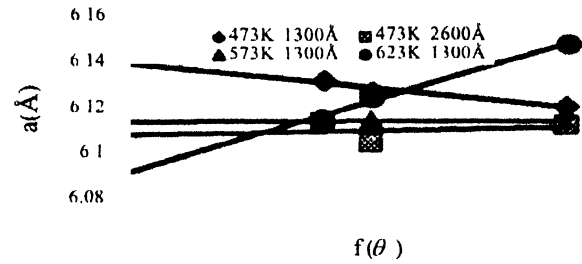

Figure 2. Nelson-Riley plot for ZnTe films for determination of lattice constant a, error function $f(\theta) = 1/2 (\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$

in the XRD measurements. It is observed that the lattice constant of the films (a) deviate from its bulk value (a_0) This shows that the deposited films are subjected to lattice strains. The lattice strains (ε) developed in the films are estimated as

$$\varepsilon = \beta_{2\theta} \cos \theta/4,$$

where $\beta_{2\theta}$ is the FWHM of [111] peak [4]. The stresses are also developed in the film due to the lattice misfit. However the stress has two components, thermal stress arising from the difference of expansion coefficient of the film and the substrate, and internal stress due to the accumulating effect of the crystallographic flaws that are built into the film during deposition. It is clearly seen that the contribution from the thermal stress is less than 5% of total stress even if the growth temperature is of the order of 623 K. Thus, the internal stress dominates in these evaporated films. The average internal stress (S) is estimated by using the relation [4].

$$S = (E_f/2\gamma) (a_0-a/a_0)$$

Where E_f and γ are Young's modulus and Poission ratio which are taken as 5.2×10^{10} N/m² and 0.33 respectively for

ZnTe films [5]. The grain sizes (D) of the films corresponding to [111] plane are estimated from usual Scherrer formula [6].

It is observed that the XRD patterns of films exhibit weak diffraction lines superimposed on a broad hump. The diffraction lines are due to crystalline phase whereas the apperence of broad hump is attributed to the presence of residual amorphous phase. Amorphous phase may predominate over the crystalline phase for films deposited at 303 K and 423 K as they exhibit a single weak diffraction line along [111] direction only. Thus, the lattice constants are calculated for the crystalline regions formed in the films deposited at 303 K and 423 K. The calculated stress corresponding to those crystalline phases is also found less for these films. In polycrystalline films, the grain boundaries play an important role in the relaxation of stresses by plastic flow, either as obstacles to dislocation or as sources and sinks in the diffusional flow. However, the stress evolution mechanism in amorphous state region may be quiet different with respect to those crystalline counterparts. In fact, the stress relaxation by plastic flow or diffusion is expected to be different in amorphous phase due to the difference in grain boundaries owing to poor orientation of crystallites with respect to the crystalline phase [7]. As the microstrain is more for these films, it is also expected that the average stress may be more than the calculated apperent values which is attributed to the predominance of interaction of amorphous phase with the crystalline structure. Amorphous phase gradually diminishes

when recrystallization process becomes prominent at higher T_s. Thus, the better crystallinity has been achieved for the deposited films above 423 K which is initiated by the pronounced surface mobility of the deposited atoms both on the substrate surface and on the deposited islands.

The calculated structural parameters at different T_s are represented in Table 1. It is observed that the estimated lattice constant of the films lies within 6.0952 Å to 6.1391 Å which is greater than the corresponding bulk lattice constant (6.09 Å) for ZnTe. The change in lattice parameters is due to the strain developed in the grains of the deposited films. Hence, the density of the films is also expected to change in accordance with the lattice parameters [8]. The grain size of the films increases at a slower rate with T_s; however, it may increase considerably with thickness (Table 1).

The average stresses of the deposited films are found to be of compressional in nature. Kisiel and Pukowska [9] also found compressive stress in vacuum evaporated ZnTe, films deposited on quartz and silicon substrates. Compressive stress is likely due to the grain boundary effect which is prominent in polycrystalline film. In compound semiconductor thin film like ZnTe the grain boundary core is relatively wider upto 1 μm due to its non-stoichiometry. This contains a large number of defects mainly arising from Zn-interstitials and Zn-vacancies in ZnTe films. Native imperfections probably migrate parallel to the film surface with their surface mobility modified by

Tabel 1. Structural parameters of ZnTe thin films depsited at 303 K to 623 K

T_s(K)	2θ (degrees)	d(Å)	[hkl] from JCPDS Data	a (Å) Calculated	a (Å) Corrected	D (Å)	$\varepsilon \times 10^{-3}$	$S(\times 10^9)$ N/m²	$\sigma (\times 10^9)$ $\Omega^{-1}m^{-1}$
303	25.2875	3.5191	[111]	6 0952	6.0952	120	3.04	0.067	0.11
423	25 2075	3.5308	[111]	6 1155	6 1155	160	2.28	-0.33	2 0
473	25.1800	3.5339	[111]	6.1208					
	41.6600	2 1662	[220]	6.1269	6.1391	180	2.03	-0.63	8.6
	49.2425	1.8489	[311]	6 1321					
573	25.2075	3.5301	[111]	6.1143					
	41.7475	2.1619	[220]	6.1147	6.1133	230	1.59	-0 30	5.4
	49.4050	1.8432	[311]	6.1132					
623	25.0650	3.5499	[111]	6.1486					
	41.6775	2.1654	[220]	6.1246	6 0905	230	1.59	0.006	0.43
	49.3900	1.8438	[311]	6.1151					
473 (t = 2600 Å)	25.2150	3.5291	[111]	6.1125					
	41.8225	2.1582	[220]	6.1043	6.1074	280	1 30	-0.22	12.3
	49.4025	1.8433	[311]	6.1135					

the substrate temperatures so that the films have a tendency to expand and thereby develop an internal compressive stress [10]. It appears that the change in average internal stress with T_S may be due to dominant recrystallization process. Thornton and Hoffman [11] suggested that the total stress generated in a thin film is a function of ratio (T_S/T_m), where T_m is the melting point of the material. In the present work, as the ratios possess a relatively higher magnitude (0.20–0.40), the stresses are relaxed by the recrystallization of strained grains into new strain-free grains along with the recovery process initiated by native imperfections. Zn-vacancies are compensated in the films as the sticking coefficient of Zn increases at high T_S and thereby improves film stoichiometry and crystallinity. The observed strain thus also decreases with the increase in T_S in the range 303 K–623 K. This decrease in strain in turn, clearly indicate the reduction of imperfections concentrations. At high T_S the excess interstital Zn atoms move from inside the crystallites to its grain boundary leading to an increase in mobility and form a better crystalline film. The film conductivity is found to be of the order of $10^{-4}\ \Omega^{-1}\ m^{-1}$ which is found to be maximum when deposited at 473 K. As the film grain size increases at a slower rate, the enhancement in mobility towards high $T_S > 473$ K is not significant. Moreover, the carrier density arising from dangling bond decreases at a faster rate in this T_S range because of possible improvement in film stoichiometry. Therefore, the decrease of film conductivity for film deposited even $T_S > 473$ K, may be the dominant effect of reduction of carrier density.

4. Conclusions

It is thus inferred from the study that the crystallinity of thermally evaporated ZnTe thin film improves with inreasing

substrate temparature. ZnTe films possess fcc zincblende structure and show a preferential orientation of crystallites along [111] direction. As the lattice misfits are considerably reduced for $T_S > 473$ K, this can minimize the structural defects in the films. An increase in film thickness may also enhance the crystallinity with higher grain size which in turn, increases the conductivity. The average stress of all films are found to be compressional in nature. The change of average stress and strain with increasing T_S is due to predominant recovery and recrystallization process. Maximum conductivity thus can be achieved by depositing ZnTe film preferably at 473 K.

Acknowledgment

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