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Synthesis of ZnTe thin film using stacked elemental layer method: structural studies

S. SHANMUGAN*, S. BALAJI, K. RAMANATHAN
Materials Laboratory, Thiagarajar Advanced Research Centre, Thiagarajar College of Engineering, Madurai – 625 015, Tamil Nadu, India

ZnTe thin films were prepared using Stacked Elemental Layer (SEL) method. The presence of Cubic and Hexagonal phases of ZnTe was confirmed by XRD technique. Cubic ZnTe phase with (111) orientation and hexagonal to cubic phase conversion was observed at 425°C. Decreased dislocation density (δ), micro strain (ε), internal stress (σ) and crystalline size (D) were observed. The observed texture coefficient (TC) value suggested that the growth of ZnTe is in (220) and (311) orientations rather than (111) orientation. The observed results were supporting the growth of ZnTe thin film using SEL method in efficient manner.

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1. Introduction

Zinc Telluride (ZnTe) is an II-VI compound semiconductor with zinc-blend structure. Due to its wide, direct band gap (2.21 to 2.26 eV); efforts have been made by many workers to produce good quality polycrystalline as well as epitaxial grown thin films of zinc chalcogenides for their effective use in many luminescent and solar cell devices. ZnTe is used as a substrate for the growth of CdTe and the heterostructures based on ZnTe and HgTe are used for infrared optics [1]. Also ZnTe has been investigated for its uses as visible light-emitting semiconductor laser [2] since it can absorb photons in the visible region without any phonon assisted mechanism that makes it useful in several electro-optic and opto-electronic applications. It has been extensively studied for application as back contact for CdTe in CdTe/CdS heterojunction solar cells [3-7].

The structure of ZnTe films is sensitive to preparation conditions. ZnTe exists into two different types (cubic: zincblende and hexagonal: wurtzite structure). The degree of crystallinity of such films are mainly depends on the structural parameters like internal and micro strain, dislocation density, crystallite size etc. and also the processing conditions. Since these parameters play a vital role in thin film fabrication, it is necessary to understand the effect of these parameters to produce good films while annealing.

A variety of preparation techniques have been reported so far to obtain device-grade ZnTe thin films. Some of them are: thermal evaporation [8], vapour phase epitaxy [9], molecular beam epitaxy [10], hot wall epitaxy [11], metallorganic vapour phase epitaxy [12], r.f. sputtering [13], electrosynthesis [14], etc. Of these methods, SEL method is one of the thermal evaporation technique, originally developed to produce $CuInSe_2$ thin films [15]. It is particularly suitable for deposition of compound semiconductor films, as it provides good control of composition. Also, it seems to be a promising method for producing highly efficient CdTe/CdS solar cells [16] and for effective doping of transition metals in CdTe thin film [17]

Quantitative determination of the different micro structural parameters like crystallite size, micro strain, dislocation density and residual stress have not yet been reported for stack Te/Zn films annealed at different temperature and are expected to influence the physicochemical properties of ZnTe films. Moreover the reduction of stress, dislocation density and increase in grain size of ZnTe films may be useful for opto-electronic applications. The objective of the present study is to find out the feasibility to form ZnTe thin film by SEL method. Also the changes in microstructural parameters with annealing temperature have been analyzed from X-ray line profile and reported.

2. Experimental techniques

Te/Zn stacks were prepared at room temperature by SEL method using PVD unit supplied by HINDHIVAC, Bangalore (model BC 300). The 5N purity Te and Zn powders were received from M/s Sigma Aldrich and used for film preparation. Sequential layer of Te followed by Zn was coated on soda lime glass. The deposition rate was maintained as 3Å/s for both Te and Zn films. To achieve the desired stochiometry, thickness of Te and Zn elemental layer was adjusted. The ratio of the thickness of elemental layers was maintained as t_{Te}/t_{Zn} = 1.95 (Te & Zn) and the thickness of Te and Zn elemental layers was maintained as 400 nm and 180 nm respectively. The distance between the substrate and source was fixed at 10 cm. To enhance

the film uniformity, rotary drive assembly was used. The stacked layers (Te/Zn/Te/Zn) were allowed to isochronal annealing from 200°C – 425°C for about 1 h in Ar gas atmosphere in a separate vacuum furnace. The structural properties were analyzed by XRD technique using CuKα radiation [λ = 1.5406 (Å)] in a Bruker D8 Advance diffractometer.

3. Results and discussion

3.1 XRD analysis

The structural properties of Te/Zn stack were analyzed using XRD technique. The observed results were presented in Fig. 1 and compared with standard JCPDS data. The XRD spectra reveals that the synthesized films are in polycrystalline nature and show that the mixed phases of Hexagonal and Orthorhombic of ZnTe were present along with elemental (Zn & Te) peaks at low annealing temperature(~200°C).

It could be observed that the crystallites were preferentially oriented with the (111) phase parallel to the substrate even at low temperature [18]. From the figure, it was noticed that the high intensity Te peaks were present along with Zn related peaks with low intensity. It is attributed to the differences of diffusion coefficients between Zn (5.808×10^{-19}) and Te (4.83×10^{-24}) at 425°C. However, the existence of Zn peaks at 425°C reveals that the non-reacted Zn atoms are still exist. It is mainly due to the top layer of the stack covered by Zn layer (Te/Zn/Te/Zn).

The XRD spectrum recorded at 200°C reveals that the synthesis temperature of ZnTe is as about 200°C. It could also be observed that the intensity of elemental peaks of Zn and Te reduces drastically with annealing temperature. It is attributed to the thermal diffusion process while temperature increases. In addition, hexagonal to cubic (ZnTe) phase conversion was observed when increase the annealing temperature from 350 to 425°C (see Fig. 1). Even though the phase changes occur, hexagonal phases of ZnTe and Te exist at high annealing temperature. It reveals that the Zn atoms are present at the surface of the stack at high annealing temperature.

The crystallite size (D) was calculated using the Debye Scherrer formula [19] from the Full-Width at Half-Maximum (FWHM) (w) and summarized in Table 1:

$$D = 0.94\lambda / w \cos\theta \qquad (1)$$

From the Table 1, it reveals that the crystallite size of the annealed films lie between 5 and 18 nm. The reduced crystallite size could be observed when the temperature increases from 350 - 425°C. It is in good agreement with the results observed by A. A. Ibrahim, et.al. [20] In addition, the lattice parameter 'a' can be evaluated from the relation:

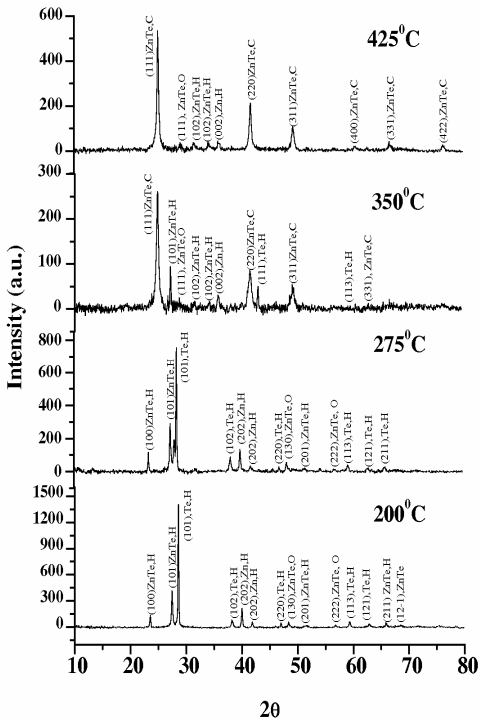
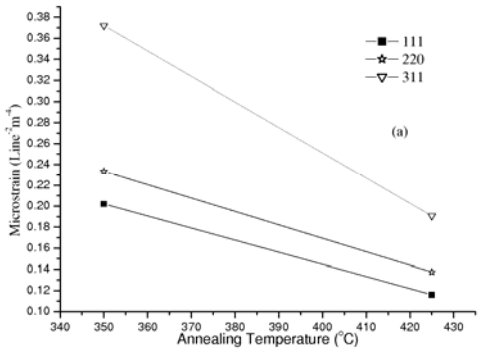
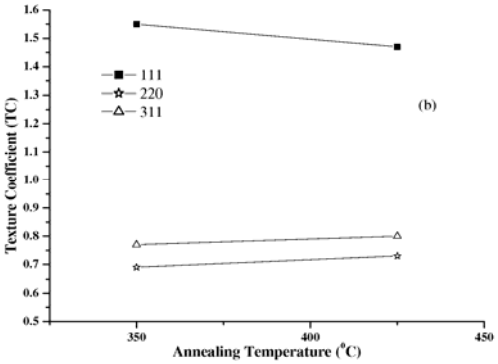


Fig. 1. XRD spectra of stacked Te and Zn layer for difference annealing temperature.



(a)



(b)

Fig. 2. Variation of micro strain (a) and Texture coefficient (b) for plane (111), (220) and (311) at different annealing temperature.

$$a^2 = d^2 (h^2 + k^2 + l^2) \quad (2)$$

where h, k, l are Miller indices. The calculated values are summarized in Table 1.

Table 1. Structural parameters of ZnTe thin film prepared by SEL method.

Annealing temperature	Orientation (hkl)	Dislocation density (x10^{15} lin/m^2)	Internal stress σ (GPa)	Lattice constant (*a*)	Micro strain ε (x 10^{-2} lin^{-2} m^{-4})	Texture coefficient (TC)	Crystallite size *D* (nm)
350	(111)	9.50	-0.02075	6.11	20.21	1.55	10.26
	(220)	12.66	-0.0196	6.12	23.33	0.69	8.89
	(311)	32.17	-0.03169	6.12	37.21	0.77	5.58
425	(111)	3.13	-0.01482	6.11	11.60	1.47	17.88
	(220)	4.40	0.00057	6.11	13.75	0.73	15.08
	(311)	8.45	-0.01648	6.11	19.07	0.80	10.88

The calculated lattice parameter value (6.11Å) is slightly larger than that of powdered ZnTe samples (6.10 Å) which indicates the presence of compressive stress in the plane of film growth possibly due to the stress developed during the annealing process. The position of Zn atom at the interstitial site in ZnTe lattice may also one of the reasons for this variation. It is known that the crystallite size is indirectly proportional to micro strain denoted as follows:

$$D = 0.94\lambda / 4\varepsilon \quad (3)$$

and the strain (ε) was calculated from the following formula

$$\varepsilon = w \cos\theta / 4 \quad (4)$$

From the Table 1, it could be observed that the reduced strain value was noticed for (111), (220) and (311) peaks and depicted the ability to grow ZnTe crystals with less defect in their preferred orientations (Fig. 2 (a)). It also reveals that the micro strain value for (220) and (311) peaks is smaller than for (111) peak. It expresses that the ZnTe crystals with (220) and (311) orientations have larger crystallite size than that with (111) orientation. To strengthen this point, the dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula [21]

$$\delta = 1 / D^2 \quad (5)$$

The calculated dislocation density was found to decrease with increase of annealing temperature and low values were obtained for films annealed at 425°C. It reveals that the stress and dislocation density decreases as the annealing temperature increases. Due to the release of stresses built-up in the layers, the reduced interplanar spacing was observed which leads to a decrease in stacking fault probability for films annealed at high temperature [22]. In another way, this may happened due to the presence of mixed phases in the stack annealed at high temperature.

In addition, the internal stress (σ) developed in the annealed films was calculated using the following formula [23]

$$\sigma = - E (d_a - d_o) / (2 d_o Y) \quad (6)$$

where d_o and d_a are the *d* spacing of bulk and thin film ZnTe (from an X-ray diffraction experiment). *E* and *Y* are the Young's modulus and the Poisson's ratio of ZnTe film respectively. The internal stress is a stress which is applied during the growth of crystals while undergoes the annealing process. From the equation-5, the nature of stress applied during the growth of crystal could be identified by the sign of the observed value. If the observed value is in positive, it represents the compressive stress and if it is negative, the tensile stress is applied during the growth process.

The calculated internal stress (residual stress) is negative for both (111) and (311) planes which depicts that the applied stress during the growth is tensile in nature**.** But the value for (220) plane was positive at high annealing temperature. It indicates that the applied stress is compressive nature. A change in applied stress from tensile to compressive could be observed with (220) ZnTe crystals. It is mainly due to the absence of (101) ZnTe peak of Hexagonal phase at higher annealing temperature. It suggests that the presence of hexagonal (101) plane of ZnTe at 2θ = 27.53 induce the tensile stress during the growth of ZnTe crystals with Cubic phase. In order to investigate the possibility of preferred orientation, the Harris analysis [24] was performed using the following relationship for the texture coefficient:

$$Pi\,(TC) = N\,(I_i/I_0) / \Sigma^{N}_{i=1}(I_i/I_0) \quad (7)$$

where P_i is the Texture Coefficient of the plane *I*, I_i is the measured intensity, I_0 is the intensity of the JCPDS powder diffraction pattern of the corresponding peak and *N* is the number of reflections considered for the analysis.

P_i is unity for each reflection in the case of a randomly oriented sample and values of P_i greater than unity indicate preferred orientation of the crystallites in that particular direction. Table 1 Summarizes the calculated value of texture coefficients and plotted in Fig. 2 (b). Note that the texture coefficient value for plane (111) decreases and the value for (311) and (220) planes increases significantly as the annealing temperature increases. It may due to the presence of Orthorhombic and Hexagonal (mixed) phases at this temperature (425°C). Therefore, our results suggest that the SEL method assists in promoting the growth of ZnTe crystals with (311) and (220) orientations than the (111) orientation [25]. The same behavior was observed with Sb doped CdTe thin film using SEL method [17].

4. Conclusions

SEL method was used to synthesize ZnTe thin film with preferred (111) orientation from their elements. Cubic ZnTe phase was observed along with some Hexagonal and Orthorhombic phases at high annealing temperature. The annealing temperature for phase changes was identified as 350-400°C from the XRD spectra. The presence of Orthorhombic and Hexagonal planes of ZnTe was the influence of structural modifications viz. change in applied stress, oriented crystal growth etc with temperature. The measured structural parameters like strain, lattice parameter, dislocation density etc. were assigned the growth behavior of ZnTe nano crystallites with their preferred orientations. The observed result was encouraging for the synthesis of ZnTe thin films with less defects by the proposed SEL method.

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*Corresponding author: sushagam@yahoo.in