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Optical Properties and Surface Morphology of Zinc Telluride Thin Films Prepared by Stacked Elemental Layer Method

Subramani SHANMUGAN *, **Devarajan MUTHARASU**

Nano Optoelectronics Research Laboratory, School of Physics, Universiti Sains Malaysia (USM), 11800, Minden, Pulau Penang, Malaysia

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ZnTe thin films were prepared by Stacking of elemental (Zn and Te) layers (SEL) followed by inert gas annealing. The optical parameters were calculated from the transmission spectra. The bandgap of the annealed samples was found between 1.95 eV and 2.06 eV. The change in film thickness after annealing was observed using cross sectional SEM image of the annealed samples. The surface morphology of the annealed Te/Zn stack was also analyzed and observed as very smooth, compact and dense surface. The prepared film was Zn rich evidenced by EDAX. The observed result encourages in pursuing the SEL method for the preparation of compound semiconductor from II-VI group materials.

Keywords: thin films, ZnTe, Stacked Elemental Layer, optical properties, surface properties.

1. INTRODUCTION

Zinc telluride (ZnTe) thin films are widely used in modern technologies of solid-state devices (light-emitting diodes, solar cells, photodetectors, etc.) because of its excellent characteristics, namely large energy bandgap, low resistivity, high transparency in visible spectral domain, [1 – 4] etc. For this compound, there is a very sensitive and complex dependence of film microstructure on preparation method and deposition conditions [5 – 8]. In this connection, many studies have recently been reported to establish the deposition conditions in order to obtain ZnTe films having a particular crystalline structure, desired optical properties and also the morphology [2 – 6, 9].

A variety of preparation techniques have been reported so far to obtain device-grade ZnTe thin films. Some of them are: thermal evaporation [5], vapour phase epitaxy [6], molecular beam epitaxy [7], hot wall epitaxy [10], metal organic vapour phase epitaxy [11], r. f. sputtering [12], electro synthesis [13] etc. Among these methods, Stacked Elemental Layer (SEL) method is a type of the thermal evaporation technique, originally developed to produce $CuInSe_2$ thin films [14]. 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 [15] and for effective doping of transition metals in CdTe thin films [16]. The optical and morphological studies are characterizing the synthesized compound thin films for suitable optoelectronic applications. In connection with this, ZnTe thin films were prepared by SEL method and the structural studies were reported earlier by the same author [17]. On continuation, the optical and surface properties of the stack (Te/Zn/Te/Zn) annealed at various temperatures are reported here.

2. EXPERIMENTAL PART

Te/Zn/Te/Zn stacks were prepared at room temperature by SEL method using Physical Vapor Deposition unit supplied by HINDHIVAC, Bangalore (model BC 300). The used 5N purity Te and Zn powders were received from M/s Sigma Aldrich. The base pressure of the chamber was $\sim 2 \times 10^{-6}$ torr. Sequential layer of Te followed by Zn was coated on soda lime glass. Before loading substrate into vacuum chamber, they were cleaned in a soap solution followed by ultrasonic cleaning in acetone for 3 min and dried under N_2 gas flow. The deposition rate and thickness of the individual layers were monitored by a quartz crystal thickness monitor equipped with a vacuum coating unit. The deposition rate was maintained as 3 Å/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. In order to get good film uniformity, the distance between the substrate and source was fixed at 10 cm. To enhance the film uniformity, rotary drive assembly was used and speed was fixed at 25 rpm.

The stacked layers (Te/Zn/Te/Zn) were allowed to isochronal annealing from 200 °C to 425 °C for about 1 h in Ar gas atmosphere in a separate vacuum furnace. The transmission spectra of all annealed stack were recorded using a Double Beam Shimatzu UV 160A spectrophotometer in the wavelength range from 200 nm to 1100 nm. The SEM with EDAX analysis was performed using HITACHI S-3400 model to study the cross sectional and morphological nature of the annealed films. ImageJ software [18] was also used to analyze the grain size and morphology of the annealed films.

3. RESULTS AND DISCUSSION

3.1. Optical Studies

Transmission spectra of all thin films annealed at various temperatures were recorded and presented in Fig. 1. It

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*Corresponding author. Tel.: +60-04-6533672; fax.: +60-04-6579150.
E-mail address: *shagan77in@yahoo.co.in* (S. Shanmugan)

reveals that the films show good transmission at higher temperature (350 °C – 425 °C). It seems to be the atomic diffusion as well as the compound formation at high annealing temperature of the stack. It is evident that the stack annealed at lower temperature shows poor transmission since the possibility of unreacted elements on the surface. The film annealed at 425 °C shows small interference pattern which is the evidence of uniform film thickness.

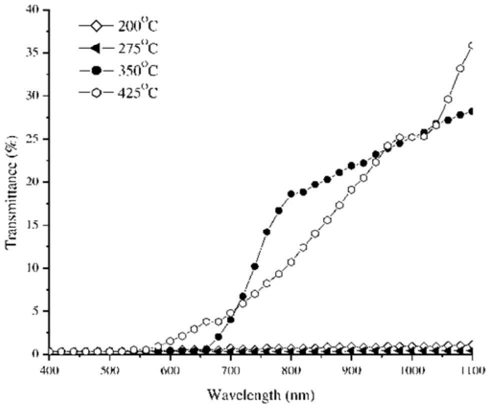


Fig. 1. Transmission spectra of annealed Te/Zn stack at various temperatures

$$\text{Te (film)} + \text{Zn (film)} \xrightarrow[\Delta\text{ (Heat)}]{\text{Vacuum annealing (Ar gas atmosphere)}} \text{ZnTe (film)}$$

From the Fig. 1, it can be observed that the transmission is high for the stack annealed at 350 °C. It is attributed to the improvement in structure as well as the stoichiometry of the films as a result of annealing. But the transmission value is comparatively small at the wavelength region from 720 nm to 950 nm for the film annealed at 425 °C. This effect may be due to presence of mixed ZnTe micro crystallites phases i. e. hexagonal, cubic and orthogonal along with trace amount of cubic Zn crystals on the surface of the stack. The detailed structural properties of ZnTe thin film synthesized from SEL method using XRD was already published in another work by the same author and reported as polycrystalline nature of annealed Te/Zn stack (see in Fig. 2) [17].

The absorption coefficient (α) was calculated from the transmission spectra using the relation [19]:

$$\alpha(h\upsilon) = \frac{4\pi k_f}{\lambda}\,. \tag{1}$$

k_f is the extinction coefficient which is calculated from the relation:

$$k_f = \frac{2.303\lambda \log\left(\dfrac{1}{T_0}\right)}{4\pi t}\,, \tag{2}$$

where T_0 is the transmission, t is thickness of the film and λ is the wavelength of the incident radiation. The absorption coefficient of annealed Te/Zn stack were calculated and plotted against photon energy as shown in Fig. 3. A wide range of absorption coefficient could be observed near the band gap region for the stack annealed at > 350 °C. This may also be due to presence of mixed phases at the surface. A sharp increase in absorption coefficient is observed on the photon energy at about 1.65 eV for the stack annealed at 350 °C. It indicates a large concentration of structural defects (especially, Te vacancies). The observed results are in good agreement with the results reported by Leiderer et al. [20].

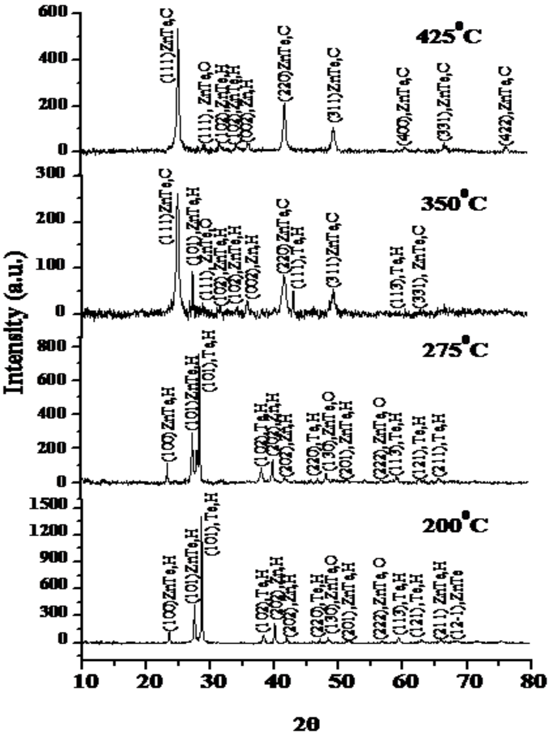


Fig. 2. XRD spectra of stacked Te and Zn layer for different annealing temperature

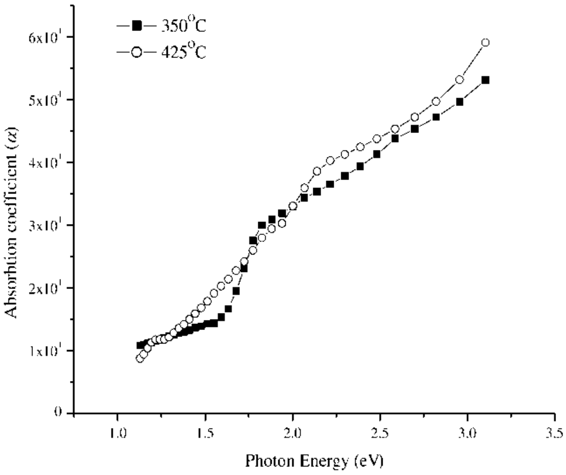


Fig. 3. Change in absorption coefficient of annealed Te/Zn stack at two different temperatures

For higher values of ($\alpha > 10^4\ \text{cm}^{-1}$) the absorption coefficient, α (where the absorption is associated with inter band transitions), the energy gap can be determined. Since ZnTe has direct transition of wide band gap, the band gap (E_g) of the annealed films was calculated from the relation:

$$\alpha(h\upsilon) = A\left(h\upsilon - E_g\right)^{\frac{1}{2}}\,, \tag{3}$$

where A is a constant. The optical band gap of direct transition (E_g) is obtained by extrapolating the square of the absorption coefficient $(\alpha h\upsilon)^2$ vs. the incident photon energy $h\upsilon$. The band gap, determined using the well-known dependence $\alpha \sim (h\upsilon - E_g)^{1/2}$ where α is the absorption coefficient, $h\upsilon$ the photon energy and E_g the band gap. Fig. 4 shows the band gap of elemental stacks annealed at two different temperatures. It is observed that the plots of $(h\upsilon)^2$ verses $h\upsilon$ for all films are mostly linear over a wide range of photon energies indicating the direct type of transitions.

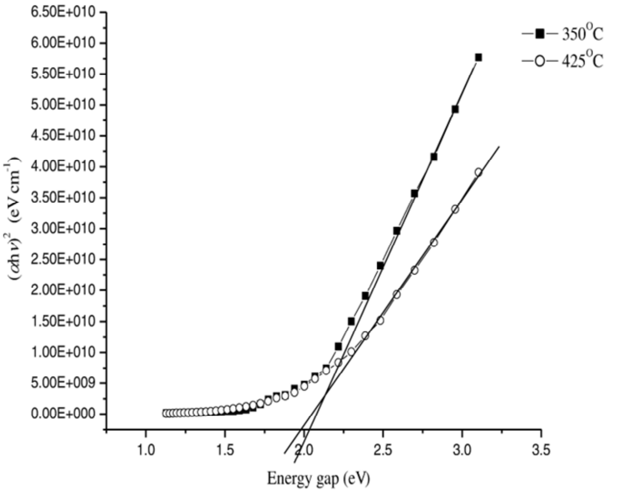


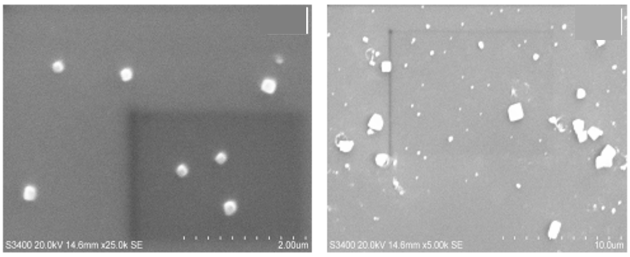
Fig. 4. Band gap variation of annealed Te/Zn stack at two different temperatures

Soundararajan et al. [21] calculated the energy gap value of ZnTe thin film prepared by thermal evaporation method. The observed energy gap (2.06 eV) for the stack annealed at 350 °C is in good agreement with the reported value (E_g = 2.09 eV) in reference [21]. The calculated E_g of polycrystalline ZnTe thin films are less than the reported value of 2.26 eV at room temperature for single crystal ZnTe [22]. The deviation in the band gap may be due to the presence of excess Te on the surface of ZnTe films [23].

The presence of elemental Te introduces a significant fraction of electronic levels in the band gap close to the valence band edge of ZnTe, with a consequent reduction of the energy associated with the direct transition [9]. The observed value is well matched with the reported value by G. I. Rusu et al. [8]. The shift in band gap from 2.06 eV to 1.95 eV may be due to the elemental diffusion into the stack at higher annealing temperature. The cause of observed red shift may be due to the increase in Zn concentrations and decrease in Te concentration on the surface of the film [21]. This could be verified by the observation of Zn related peaks in the stack annealed at 425 °C observed by the XRD spectra. It is also evidenced by the observation of excess Zn in the compositional analysis (explained in following section). The band gap of the Te/Zn stack may approach the value of 2.24 eV (pure) when the annealing time is more than one hour at 350 °C.

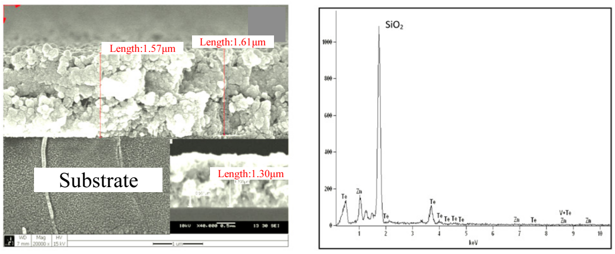
3.2. Morphological Studies

The surface morphology of the stack annealed at 350 °C and 425 °C is presented in Fig. 5, a – b. Fig. 5 shows that the observed surface is very smooth and few randomly distributed small spherical clusters are observed over the surface. This is most probably referred to the foreign particles during annealing process. It is concluded that the film surfaces are dense, smooth and have a compact in nature. The same kinds of results were observed on the surface of thin films prepared by ablation of a hot-pressed powder target ZnTe with Nd:YAG laser [24, 25]. Also, a 20 % increase in the film thickness of the stack is expected after completion of the reaction due to the difference between the molar volumes of the ZnTe compound and the Te/Zn bilayers [26]. In order to understand the change in film thickness after annealing while using the SEL method, the cross sectional image of the stacks before and after annealing was recorded and presented in Fig. 6, a.



a b

Fig. 5. SEM images of Te/Zn stack annealed at 350 °C (a) and 425 °C (b)



a b

Fig. 6. SEM Cross sectional image of the stack (a) annealed at 350 °C (inset: as grown) and (b) EDAX spectrum of Te/Zn stack (b) annealed at 425 °C

It was observed that the thickness of annealed stack was higher than that of as prepared sample. Figure 6, a, shows the thickness of as prepared thin film at around 1.30 µm (inset figure). But, the Fig. 6, a, also shows the cross sectional image of annealed stack at 350 °C and also shows the thickness of about 1.60 µm. It is found that the SEL method gives an increment in thickness when the elemental stack undergoes annealing. It is suggested that thickness of the elemental stacks after annealing must be higher than that of as prepared samples. Figure 6, b, shows the EDAX spectrum of annealed stack and also depicts the presence of only Zn and Te atoms in the stack.

The observed atomic percentage is given in Table 1. It was 73.08 % and 26.92 % for Zn and Te respectively. Hence the observed films were Zn rich. The same kind of results was observed by different author [21]. A reason for this discrepancy is clear that the standard was in the form of powder with grains in the micron range, whereas the films have very smooth surfaces and grains of the size of nano [27]. This makes the surface of the powder appear as a very rough system compared to that of the thin films. For the Te, X-ray signal with energy of 3.77 keV is not so critical, but for the Zn, X-rays with energy of only 1.009 keV which becomes a significant disturbance. The Zn L_α – X-rays are strongly absorbed by the tellurium atoms, so a surface roughness causes variations in the path length of X-rays emerging from the sample, resulting in a larger absorption of the Zn X-rays. The same kind of effect has also been observed by Bellingham et al. [28]. Another reason is may be due to the partial diffusion of Zn atom into the stack at this temperature region as well as the difference in diffusion coefficients of elements [$D_{Zn} = 0.0035 \exp(-18800/RT)$ cm^2/sec and $D_{Te} = 1.9 \cdot 10^4 \cdot \exp(-3.78\ \mathrm{eV}/kT)$]. This is also evidenced by the observation of elemental Zn peak in XRD spectrum [17].

Table 1. Atomic composition of Zn and Te in the annealed stack

Annealing temperature (°C)	Zn	Te
350	67.24	32.76
425	73.08	26.92

To enhance the study on the surface properties, the SEM image of the stack annealed at 425 °C was processed using ImageJ software and presented as a 3D image in Fig. 7. The image processing was carried out in four stages, namely de-noising, pore shape regularization, binarisation and quantification of relevant features to ascertain porosity, pore size distribution and surface texture.

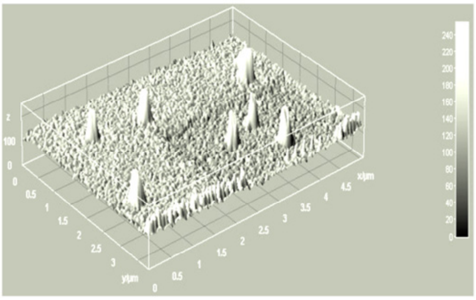


Fig. 7. 3D plot of SEM image of Te/Zn stack annealed at 425 °C using ImageJ Software

The de-noising has been carried out using a median filter and the pore shape regularization and binarisation were carried out using ‘BinariseSEM’ Java plug-in provided in the software. The particle size was determined as 20 nm by the ‘ComputeStats’ Java plug-in provided in the software. The pillar like structure is because of spherical like clusters at the surface of the annealed stack.

3.3. Electrical Studies

To understand the electrical properties in detail, the resistivity of ZnTe thin films prepared by SEL method was studied for various temperatures ranging from 30 °C to 150 °C and presented in Fig. 8. The observed resistivity was low (< 100 KΩcm^{-1}) when compared to pure ZnTe thin films. The resistivity (about 10^5 Ωcm) of these films was one order of magnitude lower than that of films prepared by evaporation (about 5.5×10^6 Ωcm) [22]. It should be noted that low resistivity is favorable for Ohmic contact. This may be due to the presence of higher percentage of Zn atoms at the surface of the annealed stack. The observed results are well match with the published results [29]. It is also confirmed by EDAX spectrum. It represents the effect of Zn particles on the resistivity of the annealed stacks. From Fig. 8, the linear behavior shows the semiconducting nature of ZnTe thin film prepared using SEL method. It is the evidence for getting binary semiconductor from the proposed SEL method.

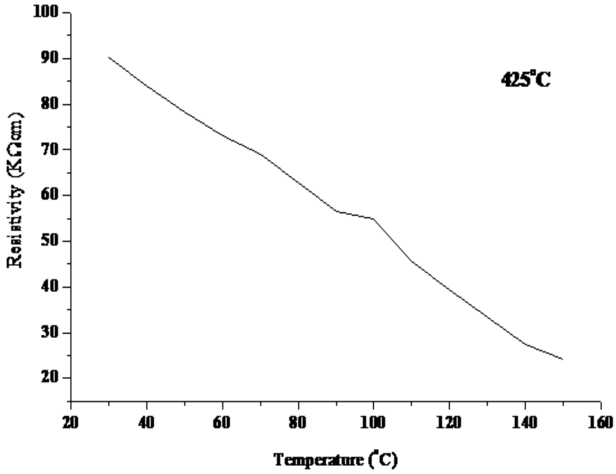


Fig. 8. Change in electrical resistivity of the Te/Zn stack annealed at 425 °C for various temperatures

4. SUMMARY AND CONCLUSIONS

ZnTe thin films were prepared using SEL method. All films after annealed at or above 350 °C have shown good optical properties. The transmission spectra were the evidence of uniform film at high annealing temperature. The optical properties were affected by the presence of mixed phases of ZnTe at the surface. The observed bandgap was in the range of 1.95 eV – 2.06 eV. The film surface was found as dense, smooth and compact in nature using SEM. EDAX suggests that the elemental compositions of the author’s samples are non-stoichiometric. Thickness of the annealed stack was higher than that of as prepared samples. Presence of nano size particles could also be evaluated from the ImageJ software. The observed results support SEL method to synthesize ZnTe thin film with good optical and surface properties.

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