Study of the Influence of Annealing Temperature on the Structural and Optical Properties of ZnTe Prepared by Vacuum Thermal Evaporation Technique

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Received in:18/March/2018, Accepted in:22/April/2018

Abstract

The ZnTe alloy was prepared as deposited thin films on the glass substrates at a thickness of 400±20 nm using vacuum evaporation technique at pressure (1×10^{-5}) mbar and room temperature. Then the thin films under vacuum (2×10^{-3} mbar) were annealing at (RT,100 and 300) °C for one hour. The structural properties were studied by using X-ray diffraction and AFM, the results show that the thin films had approached the single crystalline in the direction (111) as preferred orientation of the structure zinc-blende for cubic type, with small peaks of tellurium (Te) element for all prepared thin films. The calculated crystallite size (C_s) decreased with the increase in the annealing temperature, from (25) nm before the annealing to (21) nm after the annealing. The images of atomic force microscopy of all thin films appeared a homogenous structure and high smoothness through roughness values that increased slightly from (1.4) nm to (3.4) nm. The optical properties of the ZnTe at (RT,100 and 300) °C were studied transmittance and absorbance spectrum as a function of the wavelength. The energy gap was found about (2.4) eV for the thin films before the annealing and increased slightly to (2.5) eV after annealing at 300 °C

Keywords: ZnTe thin films, Transmittance spectra, thermal evaporation, annealing and AFM

Introduction

Zinc Telluride (ZnTe) is one of the most important semiconductor materials was used in many applications in the electronics device field. Due to its extensive contribution in the field of micro-electronics and opto-electronics applications, as the electrical, optical and structural properties of ZnTe thin films were studied over the inclusive term [1]. ZnTe is grey or brownish-red powder, has a cubic and hexagonal crystal structure, because of lattice matching, it can grow on AlSb, GaSb, InAs, and PbSe substrates, it can also grow on gallium arsenide but in that case there will be some lattice mismatch [2]. Zinc telluride can be classed to the II–VI group of semiconductor compounds and like other family of the group, the material has a direct band gap of 2.26eV at RT [2-3], which corresponds to the pure green region of the electromagnetic spectra, and hence it is seen as a potential material for the fabrication of green LEDs. ZnTe has been used in γ-ray detectors, solar cells [4-5] switching devices and optoelectronic devices [2]. ZnTe thin films can be fabricated by using closed space sublimation (CSS) technique [6], sputtering [7], electro-deposition process[8], electron beam evaporation[9] and thermal vacuum evaporation method[10].In the present paper an attempt has been made to study the effect of annealing temperature on the structural and optical properties ZnTe thin films prepared by vacuum.

Experimental

To prepare ZnTe alloy, appropriate atomic percentage of high purity (99.99%).Zinc (Zn) and Tellurium (Te) were taken by using sensitive electric balance type (Mettler H35 AR). These elements were put in a clean and dry quartz ampoule to prepare ZnTe. Then the ampoule was linked by specific design to the vacuum unit, when the pressure reached $2x10^{-3}$ mbar, the ampoule was sealed, then the ampoule was heated for (1200 ^{o}C) using furnace, and kept at the temperature for 1 hour. After that the ampoule was cooled down in furnace and then broken to bring out the alloy.

ZnTe films were deposited on well cleaned glass substrates by thermally evaporating powder ZnTe in a molybdenum boat. A pressure of about (1×10^{-5}) mbar was maintained within the vacuum chamber at the time of deposition. The deposition rate was maintained at about 33 nm/min. The obtained films were uniform and had good adhesion to the substrate. Typical ZnTe films having thickness at 400±20 nm were used for characterizations. Then the thin films ZnTe were annealing at 100 ° C and 300 ° C for an hour under vacuum of 10^{-3} mbar. The X-ray diffraction (XRD) studies of the films were performed by (SHIMADZU Japan-XRD600) automatic Diffract meter using the CuK_{α} radiations (λ=1.54059 Å) in the range of 2θ between 10° and 120°. Surface morphology was studied using Atomic force microscopy (AFM) measurements with specifications (SPM model AA 3000 Angstrom Advanced Lns., USA) to determine the Nano-crystalline topography and grain size of the films. Optical transmission measurements were performed with (UV/Visible 1800 spectrophotometer).

Results and Discussion

Structural properties

Figure (1) shows the XRD pattern of the prepared ZnTe powder, which has a polycrystalline structure, and the positions of these peaks were compared with the ICDD card of this compound and its component elements. The ZnTe is formed in two phases, cubic phase and hexagonal, and with different crystalline directions as indicated above each peak. Also, when comparing the number and intensity of peaks, we can conclude that the dominant phase is the cubic phase and the direction (111). In addition, weak peaks of the elements (Zn, Te) are observed, which may be due to heterogeneity due to the weight differences in the preparation of the alloy and can be considered experimental errors.

Table (1) shows ZnTe alloy and its structural properties, which include ICDD card information. It is noted from the table that there is a great match between the top positions between the prepared alloy and the special information card for the cubic structure. The crystallite size (Cs) was determined from X-ray diffraction data using the Scherer's equation [10].

$$C_S = \frac{0.94\lambda}{B_{(FWHM)}\cos\theta} \quad \text{.....(1)}$$

Where λ is wave length of XRD, β is full width half maxima and θ the diffraction angle. The calculated crystalline size (Cs) has a Nano-scale dimension, and the largest measured magnitude at direction (111) corresponds to the lowest crystalline size of 35.8 nm. Since the high intensity of any peaks explains that most of the crystals formed have the same direction (hkl) (ie: increase the number of crystals at the direction of hkl). Considering that all of them reflect X-rays in the same direction, so the particle size increases with increasing intensity and decreasing the value of FWHM .The distance between the crystalline planar (d_{hkl}) which corresponds to the results of the standard information card, is calculated using the Bragg equation [11].

$$n\lambda = 2d_{hkl}\sin\theta \quad \text{..... (2)}$$

Where (n) is an integer and it is the order of reflection, d_{hkl} is the distance between the lattice planes, and (hkl) are Milles indices

Figure (2) shows XRD and the effect of temperature before and after the annealing of thin films deposition on glass bases at 100 °C and 300 °C for an hour. We observed that all prepared thin films close to the single crystalline structure of the cubic type at a crystallization direction (111) and high intensity[10], with the disappearance of the hexagonal phase. The absence of different crystalline orientation in the alloy and the existing of a single crystalline growth gives great uniformity and decreases the crystalline defects of the thin films deposition[11], in addition to decreasing the crystallite size and increasing the diffraction intensity of the effect of the annealing, which means an increase in grain size as shown in Table(2).

We also show the appearance of weak peaks of the tellurium (Te) at diffraction angles (2θ) (22.77, 27.78, 40.34, 43.32), as shown in figure (2) which explains the positive conductivity (p-type) (ZnTe) for the presence of the vacancy of the zinc element in ZnTe structure. This is consistent with the researcher [9].

Table (1): The results obtained from XRDfor zn Te alloy

	XRD				ICDD				
	2 theta (deg.)	d(°A)	FWHM (deg.)	Cs(nm)	2 theta (deg.)	d(°A)	(hkl)	lattice const.(°A)	card No.
C-ZnTe	25.284	3.520	0.2273	35.822	25.259	3.523	(111)	6.103	15-0746
	41.867	2.156	0.2003	42.467	41.805	2.159	(220)		
	49.523	1.839	0.1991	43.942	49.496	1.840	(311)		
	66.774	1.400	0.1782	53.388	66.745	1.400	(331)		
H-ZnTe	27.597	3.230	0.2269	36.056	26.914	3.310	(101)	a=4.31 b=7.09	19-1482
	34.441	2.602	0.1540	54.011	34.854	2.572	(102)		
	56.652	1.623	0.2267	39.809	55.585	1.652	(202)		
	62.877	1.477	0.1600	58.192	63.540	1.463	(203)		
H-Te	38.287	2.349	0.3167	26.554	38.260	2.350	(102)	a=4.458 b=5.927	36-1452
	40.484	2.226	0.2600	32.568	40.445	2.228	(110)		
H-Zn	36.294	2.473	0.1792	46.655	36.296	2.473	(002)	a=2.67 b=4.95	04-0831

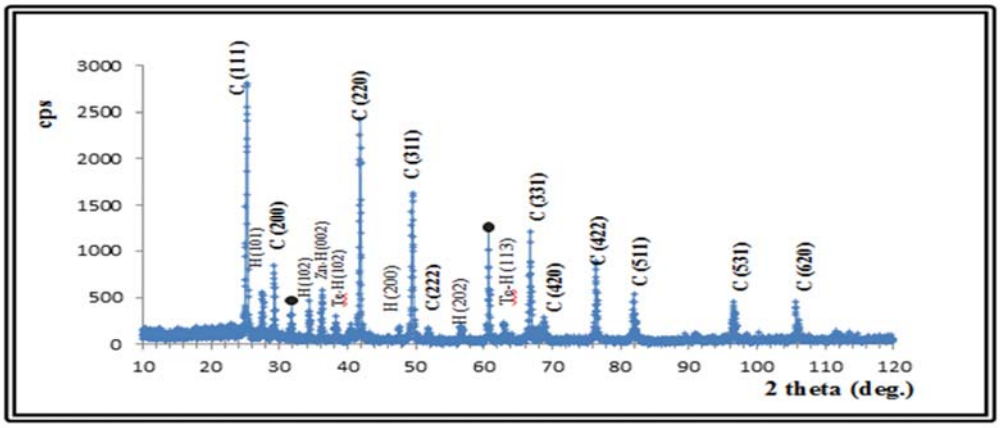

Figure (1): X-ray diffractior pattern of the zn te alloy

Table (2) 2θ, d,FWHM,hkl and Cs values of ZnTe

substrate	T °C	2Theta (deg.)	d(°A)	FWHM (deg.)	hkl	Cs nm
glass	RT	25.267	3.522	0.315	111	25.84
	100	25.271	3.521	0.316	111	25.75
	300	25.235	3.526	0.379	111	21.47

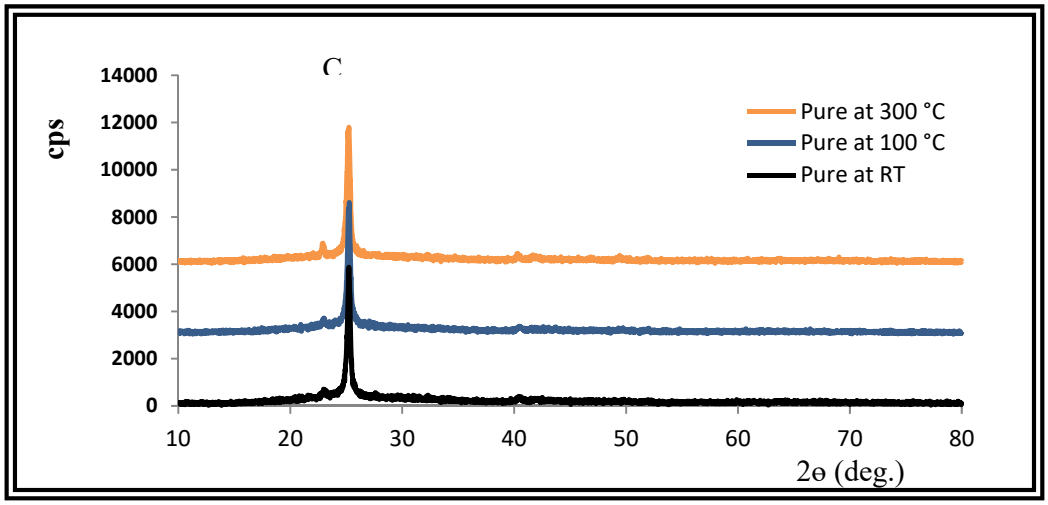

Figure (2): XRD of the ZnTe / glass thin films before and after annealing at

Atomic Force Microscopy Measurement

Atomic Force Microscopy (AFM) was used to study the roughness of the surface nature of the thin films and the effect of the annealing on the homogeneity and uniformity of these surfaces. In addition, it has the ability to show and analyze thin films surfaces and to give accurate statistical values on the rate of grain size and surface roughness based on the root mean square (r.m.s.)

Figure (3) shows three-dimensional (AFM) images of pure thin films annealing at 100 °C and non-annealing. We observe the formation of nanotubes structure. Some of which are hollow with homogeneous heights up to (38 nm). Figure (4)shows two dimensional images of AFM and three dimensions of pure thin films prepared at room temperature RT and annealing (100 and 300) ºC for a surface scan rate of (1.55µm × 1.55µm), it appears that the grain size measured by this technique is almost constant at the limit of (46 nm), although the process of annealing is increasing in the roughness factor of the pure thin films at RT from (1.39 nm) to (3.45 nm) for the pure thin films annealing at (300 ºC), which is a small amount that is considered to be an indicator of the smoothness and homogeneity of the thin films[12].

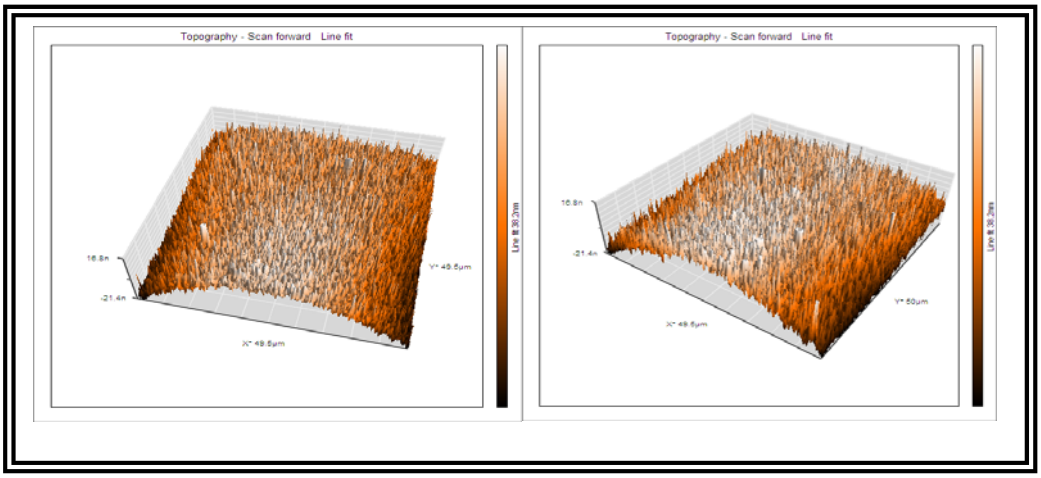

Figure (3): AFM images of pure ZnTe thin films at RT and annealing 100 ºC. For thickness 400 nm on surface area (50µm × 50µm)

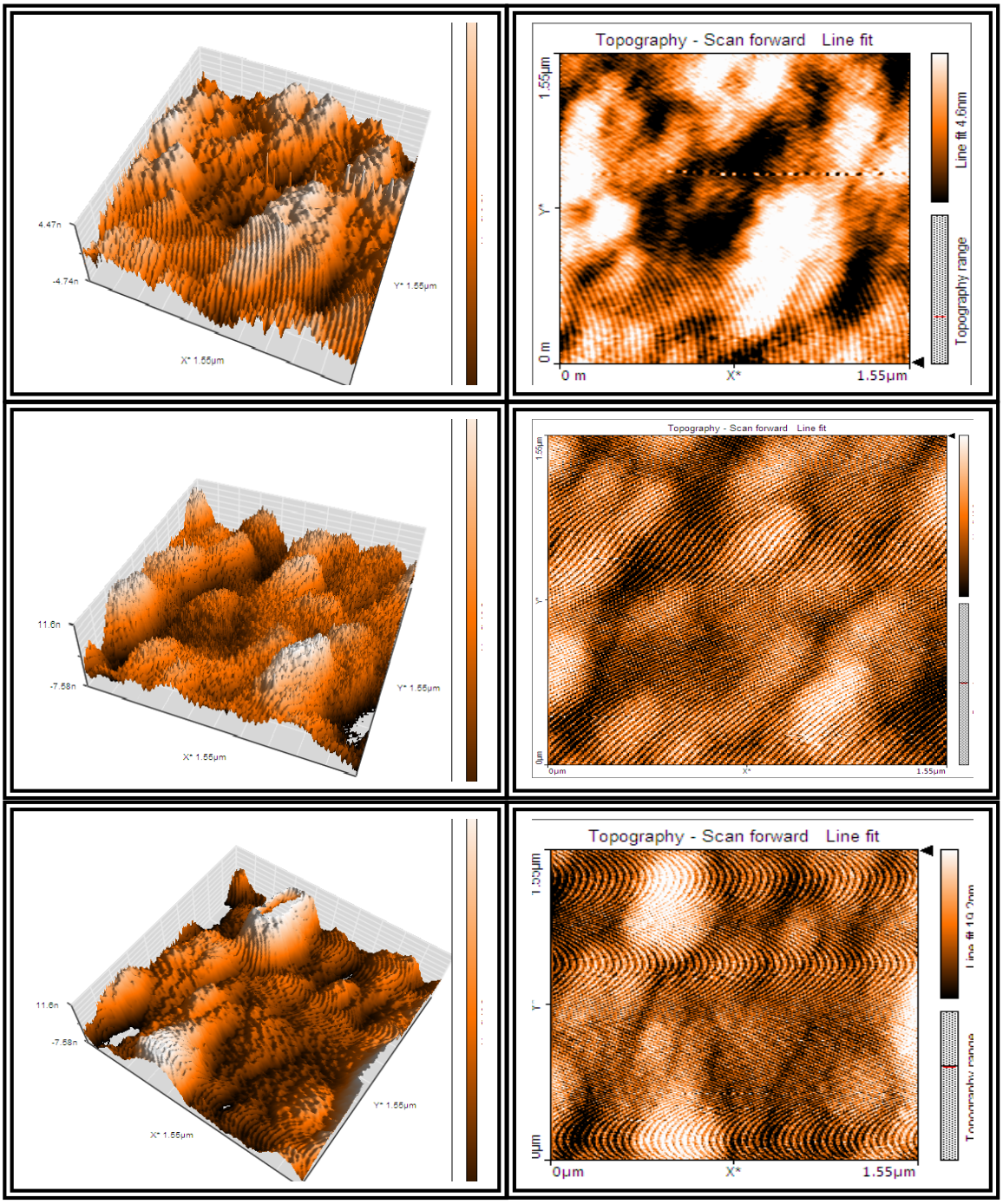

Figure (4): Represent the AFM image of the pure thin films at room temperature (RT) and the annealing at (100,300) ºC

Optical properties

The absorbance and transmittance spectra were measured as a wavelength function in the spectral region (300-1100) nm at thickness 400 nm for pure ZnTe films at room temperature and for annealing (100 and 300) ºC as shown in figure. (5). It can be seen from the figure the effect of increasing the temperature of the annealing on the thin films preparation, through the sharp drop in the absorption spectral for the exponential absorption area within the range (400 to 600) nm for the ZnTe films at 300 °C. In addition to the shift of the absorption spectrum

towards the short wavelengths, leading to an increase in the energy gap which caused a decrease in absorption. For the close link between the intensity of electronic transitions and the energy gap. The larger the energy gap the electronic intensity moving from the valence band to the conduction band decreases, resulting in decreased absorption. This is evident from seeing increased transmittance spectrum from 15% to 50% at 850 nm wavelength for the annealing films from (100 to 300) °C

The fundamental absorption which compatible with electron excitation from valence band to conduction band, it is used to find nature and value of the energy gap. The energy gap (E_g) of the ZnTe thin films is calculated using the expression[6,13]:

$$\alpha h\nu = B\,(h\nu - E_g)^{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where: B is constant, α (cm^{-1}) is the absorption coefficient, hν is the photon energy and E_g (eV) is the energy gap. The parameter (r) is determined by the optical transition involved in the absorption process, it equals (r=1/2) for the allowed direct and indirect transition (r=2) in the electronic band structure. The energy gap (E_g) was obtained from the intersection of the photon energy axis by the straight line of the curve $(\alpha h\nu)^2$ versus (hν) plot as shown in Figure(6), this relationship is related to ZnTe thin films non-annealing and annealing (100,300) °C. In general, the energy gap in thermal treatment is increasing from (2.4eV) for thin films non-annealing to 2.5 eV for ZnTe annealing (300 °C). This may be due to the fact that thermal treatment has improved crystalline structure and reduced the structural defects of removing localization state in the energy gap, thus increasing the energy gap.[13]

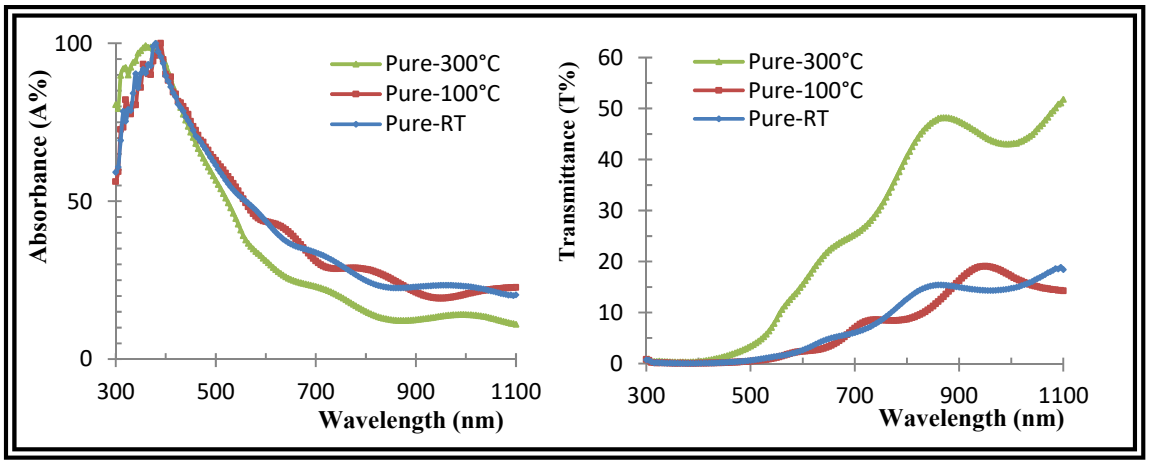

Figure (5): Absorbance and Transmittance spectra of ZnTe at room temperature and the annealing (100,300) °C

Conclusions

In the present work, the effect of annealing temperature on the structure and optical properties of ZnTe films were prepared by thermal evaporation method are studied. From XRD study it was found that all prepared thin films close to the single crystalline structure of the cubic type at a crystallization direction (111) and high intensity, with the absence of the hexagonal phase and others different direction in the alloy, as well as the continued existence of weak peaks of element Te. This explains the positive conductivity (p-type) of these thin films. The calculated crystallite size (C.S) was decreased with the increase of the annealing temperature. AFM images indicated high smooth surfaces with small RMS roughness values and an increase in the roughness with the increase of the annealing. The optical band gap (E_g) increases with the increased temperature of the annealing; this may be due to the fact that

thermal treatment has improved crystalline structure and reduced the structural defects of removing localization state in the energy gap.

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