Substrate temperature dependence of optical and morphological properties of ZnTe nanoparticles thin films

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Abstract:

ZnTe nanoparticles thin films were prepared at different substrate temperature (325, 425,525,625K) on a glass substrate by using Pulsed Laser deposition technique (PLD) under vacuum about 10^{-5} Torr. The Nd-Yag Q-Switch laser with wave length (1064 nm), frequency (5 Hz), and fluency (0.477 J / cm^2) were employed to deposit ZnTe thin films. The as deposited of ZnTe nanoparticles thin films were investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Electron dispersion X-ray (EDX), Atomic force microscopy (AFM) and UV-VIS Spectrophotometer. XRD investigations confirmed the increasing in the crystallite size about (42.64, ٤٤,٠٢, ٨٢,٦٦ and 86.64nm) with increase substrate temperature in the range (325K, 425K, 525K and 625K), respectively.

Keywords: Pulsed laser deposition (PLD), ZnTe thin films, nanoparticles, substarte temperature, optical and morphological properties.

1. Introduction

Due to the stability of fundamental structural, of family of group II–VI semiconductors has been widely studied, electrical and optical properties for use in thin film solar cells, photodetectors and light emitting diodes (LEDs) [1-3]. Crystalline ZnTe has a with low electron affinity of 3.53 eV with direct bandgap of 2.21 to 2.26 eV at room temperature [4, 5] ZnTe thin films have been prepared by different techniques, including pulsed laser deposition (PLD) [6], magnetron sputtering [7], thermal evaporation

[8-10], molecular beam epitaxy (MBE) [11], electron beam [12], closed space sublimation (CSS) [13], electro-deposition [14]. Pulsed laser deposition technology is of great importance for use in many important fields like biochemistry by preparing nanoparticles conjugated
partially purified tannase [15], preparation of nanoparticles in different liquids involved in the manufacture of solar cells [16], preferment of thin film coatings for medical device manufacturing, mechanical engineering, microsystems technology or optics on a short timescale. For this compound, there is a sensitive and complex dependence of film microstructure on preparation method and deposition conditions [17-20]. In this connection, many studies have been established deposition conditions in order to obtain ZnTe films having a particular crystalline structure and morphology [21-23]. This research included a comprehensive report on the manufacture of zinc telluride nanoparticles thin films by pulse laser deposition technique with different deposition temperatures and their effects on the structural and optical properties of these films.

2. Experimental procedure

2.1. ZnTe target preparation

A weight from elements of the Zinc and Tellruide powder were used to prepare (Zn-Te) alloy. By taking atomic ratios from the elements according to the atomic weights for each element using sensitive electrical balance having four decimal ranks, The relative atomic weight of the element i.e. : Zn atomic weight = 65.37 (3.3 21.8215 % mass from alloy) Te atomic weight = 127.6 (1.7 23.945 % mass from alloy) The Equation used to determine the weight of each element in the alloy

$5 = (a + b) * m_a/m_a$, $m_a =$ Atomic weight of an element in the alloy, w_a = Atomic weight of an alloy, a = the first element , b =the second element. After that putting these materials inside a clean quartz tube interior diameter (1.1cm) and (10 cm) length. The tube good cleaned in the distilled water, followed by alcohol and then heated it for high temperatures in order to remove any blemishes. It is a necessary remark that the length of this tube must match with mixture weight to prevent explosion during formative operations of meltdown assembled because of vapor pressure of these elements, afterwards put this tube in vacuum

system (about 10^{-2} Torr) then closed it by welding using oxyacetylene flame where this operation occurs to prevent oxidation of the elements during melting. Then, the evacuated tube was put in the furnace where it reached maximum temperature at 1373 K, the vacuum tube heats up to 1125K for three hours with shaking for (15 Sec every half hour) in order to have homogeneous mixture, then turn off the furnace and let tube coold down. After that break the tube and then compressing the powder and heated to 1173K for five hours in order to have homogeneity mixture. ZnTe powder, prepared through the grind alloy and It is produced pellet by pressing squeeze at (13) ton. The producing pellet of ZnTe with dimensions (2 cm x 0.1 cm), is a homogeneous target as possible to ensure agood quality of the deposition.

2.2. ZnTe NPs thin films deposition

The PLD was carried out by using a Q-switched Nd: YAG laser with wave length (1064 nm), no. shots of laser about 5000p, laser flounce (4.77 J/cm^2) and spot diameter of incident laser (d=3mm) on target with an angle about 45^o . The repetition rate of the laser beam was 5 Hz. The target and substrate rotated with 6 rpm by using DC motor to avoid drilling effect. The chamber of substrate and target holder evacuated to a pressure about 10^{-5} mbar. All samples of ZnTe NPs prepared at different substrate temperature from 325K to 625K. The thicknesses of the films were 50 nm for each 1500 pulse after deposition.

3. Stractural and morphological investigations

3.1. XRD measurements:

ZnTe target was investigated by X-ray diffraction and found that ZnTe exhibits cubic phase as shown in figure (1). X-ray diffraction patterns of ZnTe NPs thin films deposited on glass substrates are shown in Fig. 2. A strong peak is observed around at 2θ = 25.48o which corresponds to preferred orientation along (111) plane of cubic phase. It is good agreement with the standard JCPDS-ICDD (01-0582) data of ZnTe. The intensity of the peak (111) increases and the full width at half maximum (FWHM) of the films decreases with the increase of substrate temperature from 325K to 625K.

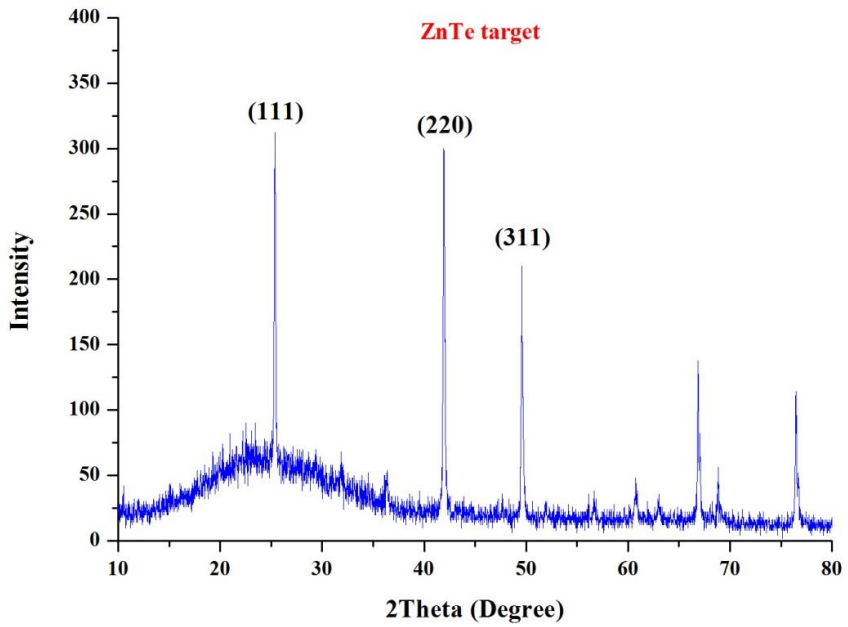


Fig. 1. XRD investigation of ZnTe target.

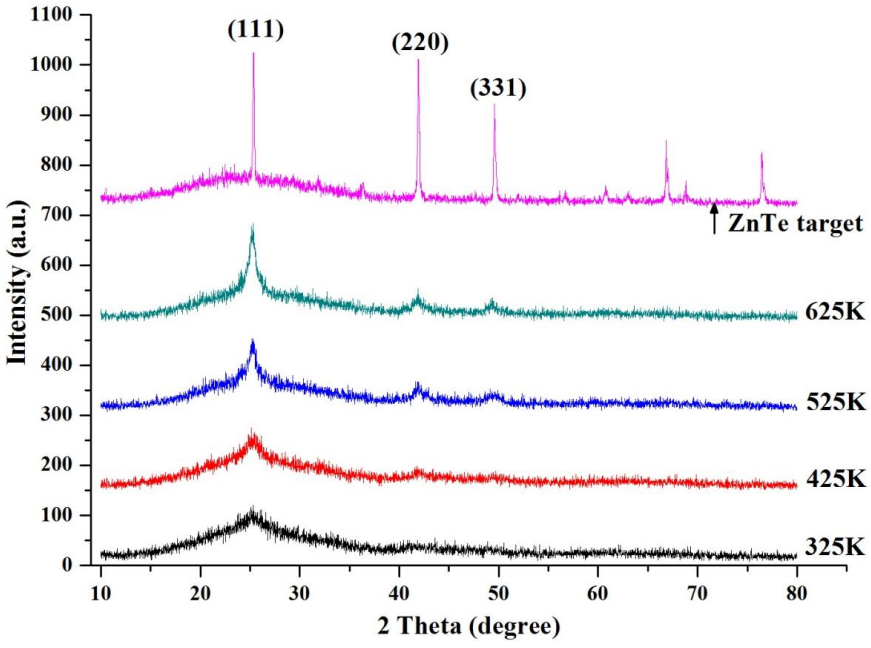


Fig. 2. XRD investigations of ZnTe NPs thin films prepared by PLD at different substrate temperature.

The increase in peak intensity and decrease of FWHM is due to the improvement in the crystallinity of the films with increases substrate temperatures.

The average crystallite size (D) of the films is estimated from Scherrer formula [24]:

$$D = \frac{k\lambda}{\beta cos\theta} \quad \ldots\ldots(1)$$

Where k is constant$0.89 \leq k \leq 1$, β is the full width at half maximum of (111) peak.

λ is the wavelength of the X-ray and θ is diffraction angle.
Also, the dislocation density for cubic ZnTe thin films is estimated from Williamson and Smallman's formula [25]:

$$\delta = \frac{n}{D^2} \quad lin.m^{-2} \quad \ldots.(2)$$

where n is a factor, which when equal to unity gives the minimum dislocation density and D is the average crystallite size. By using eq. (1) and from the figure (3) we can observed that the crystallite size of the films increases with increased substrate temperature and reached a maximum value of 86.64 nm at substrate temperature of 625K.

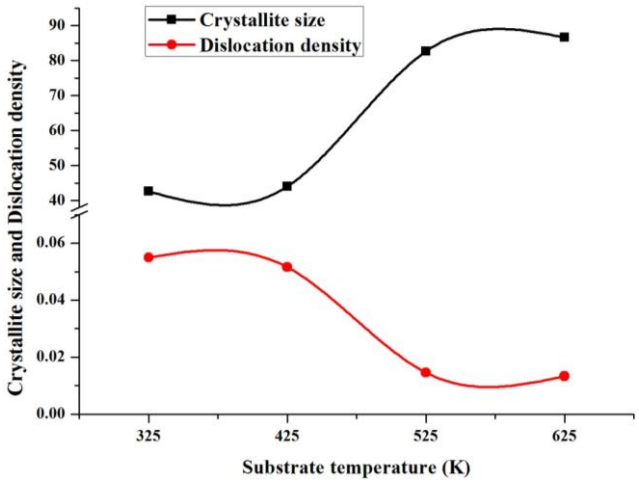


Fig. 3. Crystallit size and dislocation density of ZnTe NPs thin films at different substarte temperature.

Due to the increase of crystallite size with substrate temperature, the defect in the lattice is decreased, which in turn reduces the dislocation density estimated by eq. (2). This results are agreement with [26, 27].

The microstrain (∈) developed in the ZnTe films was calculated by using the relation.

$$\in = \frac{\boldsymbol{\beta cos\theta}}{\mathbf{4}} \quad \boldsymbol{lin^{-2}.m^{-4}} \quad \ldots\ldots (\mathbf{3})$$

The decrease of micro stain (ε) that estimated by eq.(3) and dislocation density (δ) at higher substrate temperatures may be due to the movement of interstitial Zn atoms from inside the crystallites to its grain boundary which dissipate leading to reduction in the concentration of lattice imperfections. The microstructural parameters of ZnTe thin films deposited at different substrate temperatures are given in table 1.

Table (1): Dependence of microstractural parameters of ZnTe NPs thin films on substrate temperature.

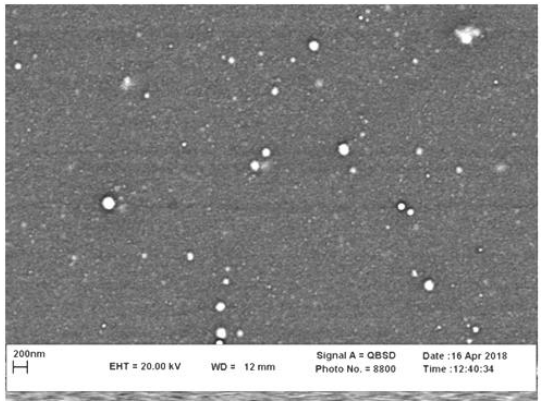
Substrate temperature (K)	Crystallite size (nm)	Micro-starin*10^{-3} (($lin^{-2}.m^{-4}$)	Dislocation density*10^{-2} (($lin.m^{-2}$)
325	42.64043	8.09	5.50
425	44.02574	7.83	5.159
525	82.66217	4.17	1.463
625	86.64267	3.98	1.332

The results obtained are in good agreement with the previous reported literature [28].

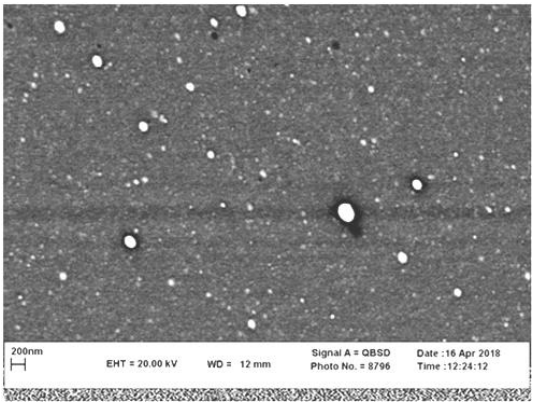
3.2. SEM measurements:

By SEM (S-2700 from Hitachi), the surfaces of the ZnTe NPs thin films were analyzed. As shown in figure, all images of SEM are represented in (S-2700, SE, 15 keV), (S-4800, BSE and SE, 1 keV). The SEM analysis show differences in the morphology and microstructure of the ZnTe NPs films prepared at different substarte temperatures. films, prepared 625K and 525K substrate temperatures have low rougher surface, while the surface of the films prepared 325K and 425K are rather rougher. Through SEM measurements, the nature of the nanoparticles of the films prepared

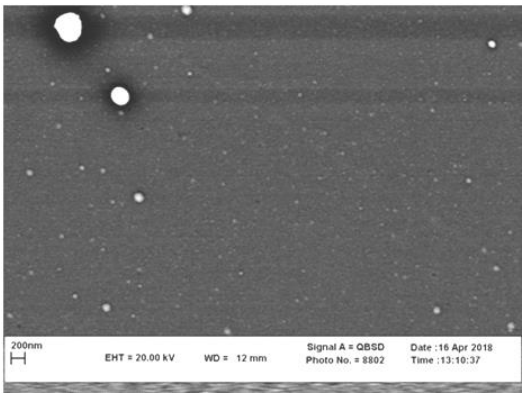
from zinc-teloride were spherical shape as shown in the figure (4). The spherical shape of nanoparticles is the result of heating ultra-secondary layer near the surface. If the secondary layer of target is heated faster than the area near the surface of target, the liquid droplets can eject from the molten layer.



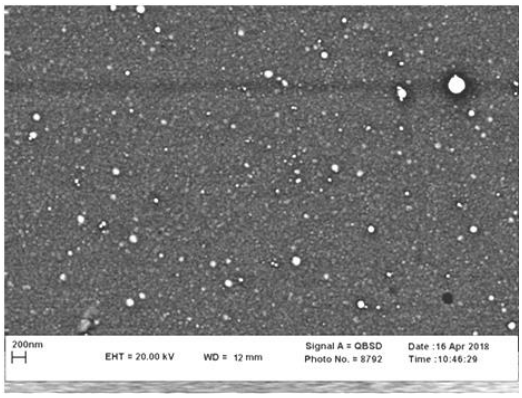
325K



425K



525K



625K

Fig.4. SEM surface images of PLD ZnTe NPs thin films on glass substrate formed varies substrate temperature (325K, 425K, 525K and 625K).

These particles are within the nanoscale with the spherical shape and have a smooth surface. As for the small particles, they are caused by the super saturation of the vapors formed above the surface of the target material. This results agreement with [29]. The composition of the elements of the prepared films by PLD technique with a wavelength of 1064 nm were studied. The primary composition of the ZnTe target, which was prepared in the present work, was Zn:Te=0.49:0.51. The EDX measurements were obtained using the SEM (S-2700 Hitachi) supplied with the energy-

dispersive x-ray spectrometer (EDAX 9100). Through SIM images, the composition of the elements was measured as indicated in figure(5).

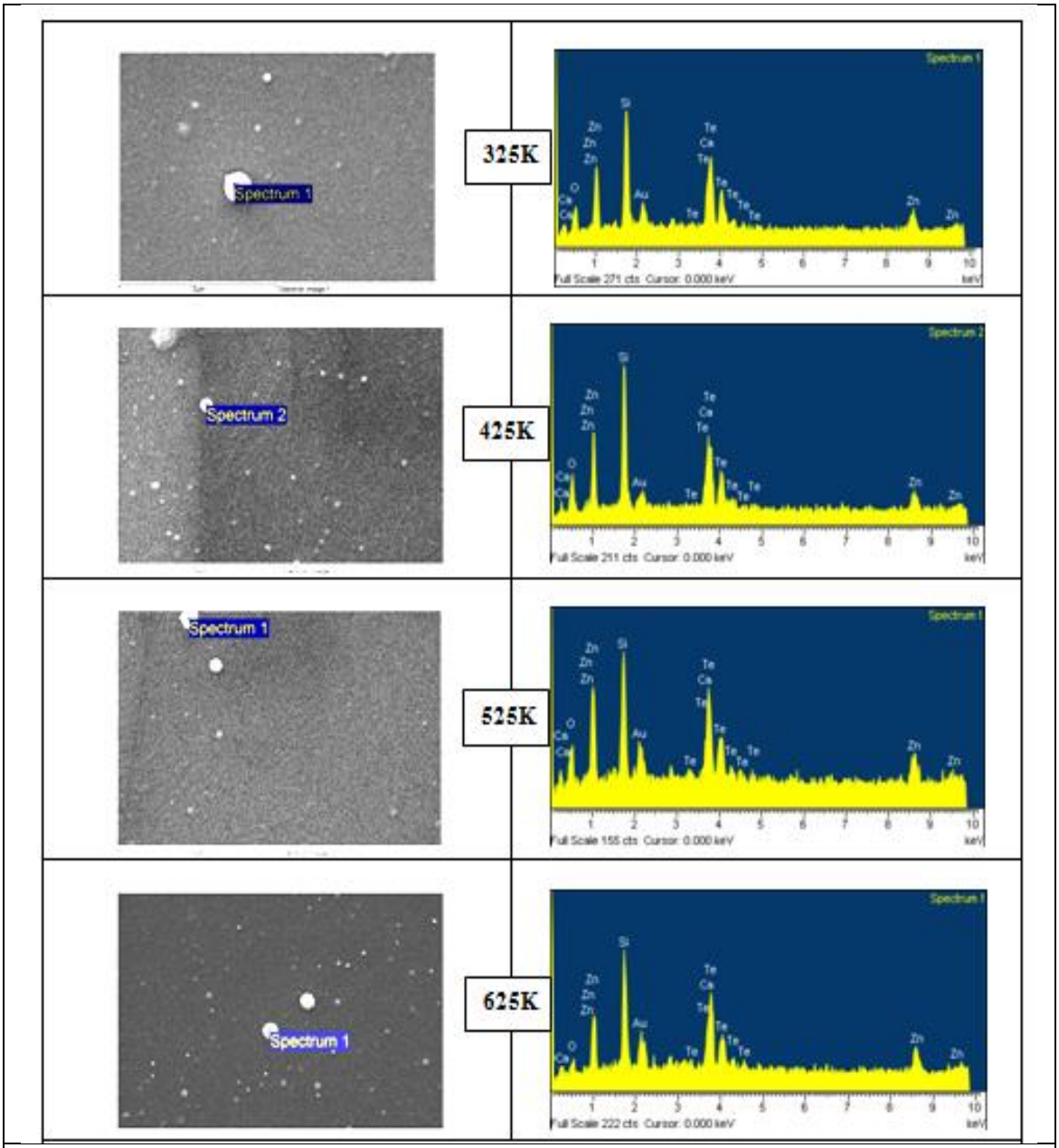


Fig.5. SEM-EDX spectra obtained by EDX elemental analysis of PLD ZnTe NPs thin films on glass substrate at different substarte temperatures.

The results obtained using EDX for the ratio of zinc /teloride for the ZnTe films prapered at different substarte temperaturs (325, 425,525 and 625K) can be illustrated from the figure (6).

The results show that the films are prepared at different substrate temperatures (325, 425, 525 and 625K) display Zn-reductions.

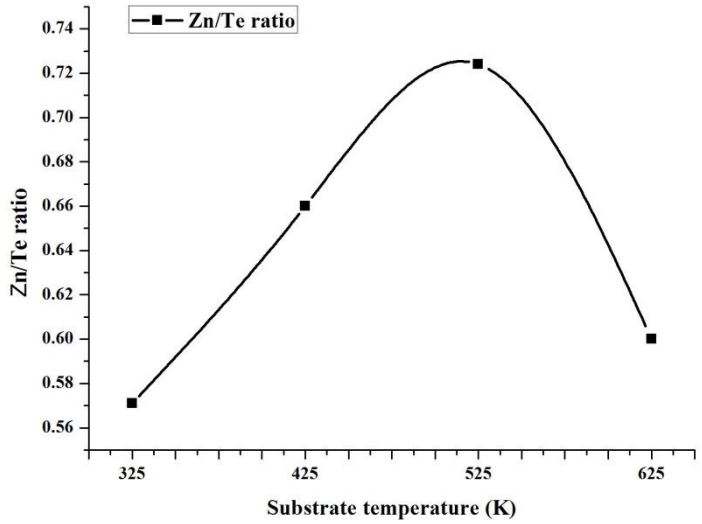


Fig.6. Composition distributions of PLD ZnTeNPs thin films on glass substarte prepared at 325K, 425K, 525K and 625K: Zn/Te ratio versus substrate temperature.

The composition is temperature dependent, and improves with increasese deposition temperature and reached maximum at 525K.

3.3. Film Surface Characterization by AFM

The AFM investigations explained that the increasing in the substrate temperature in the range about (325, 425, 525 and 625K) lead to increase in the grain size of ZnTe NPs thin films with (45.86, 49.99, 67.46 and 69.61 nm) respectively, as shown in figure (7). Also, it is possible to distinguish the voids of the films prepared with increasing substrate temperature in the range about (325, 425, 525 and 625K) deu to the slight decrease in the packing density of the films and that explained by AFM 2D in the figure (8). The surface of the ZnTe film deposited at hghier substarte temperature (625K) is rather compact and smooth, showing a granular structure with well-defined grain boundaries. Also, as results for increasing substarte temperature that the film at (625K) less rough. The decreases in roughness with the substrate temperature agreement with [30, 31, 32].

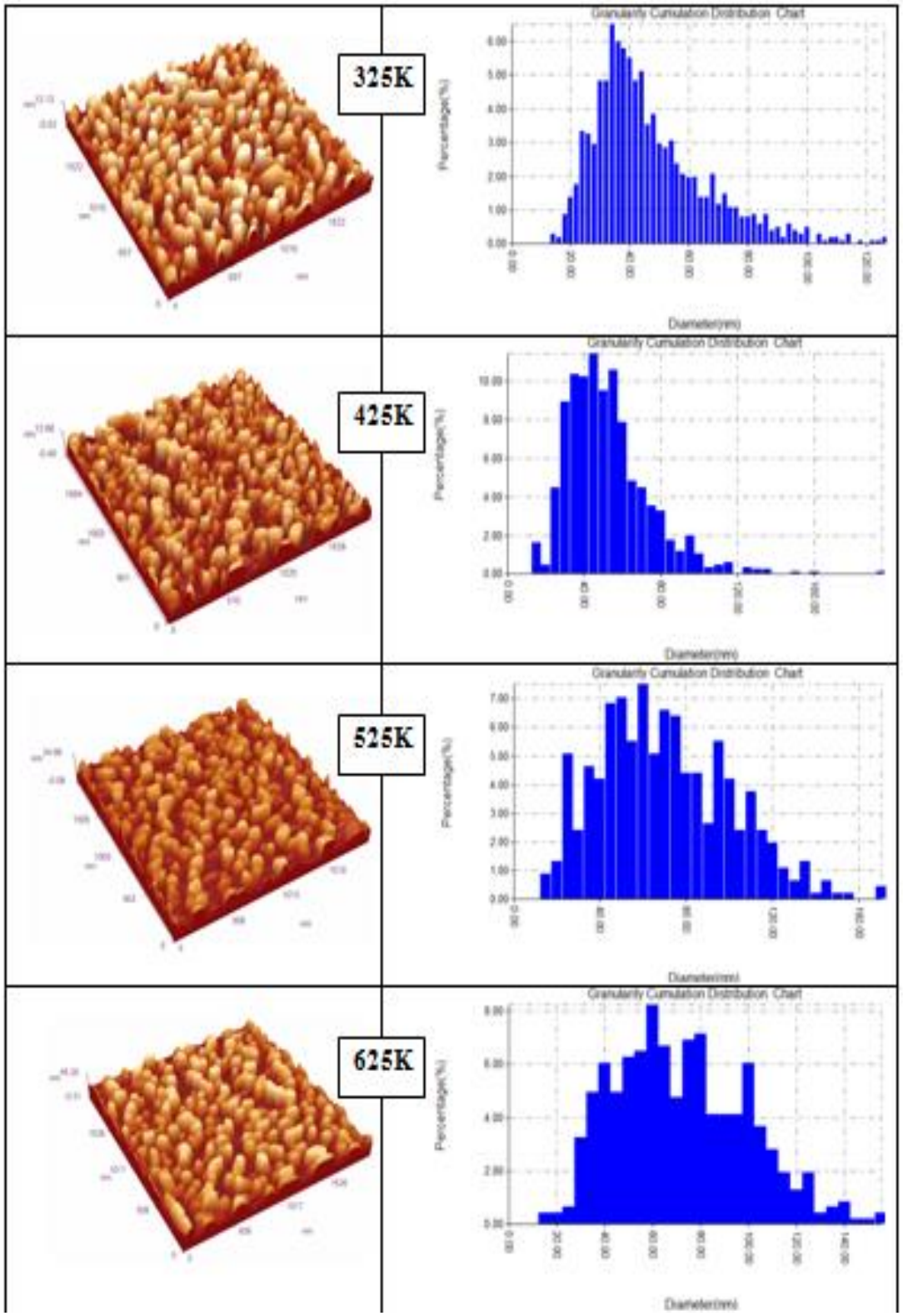


Fig.7. AFM images of ZnTeNPs thin films on glass substrate prepared by PLD at 325K, 425K, 525K and 625K.

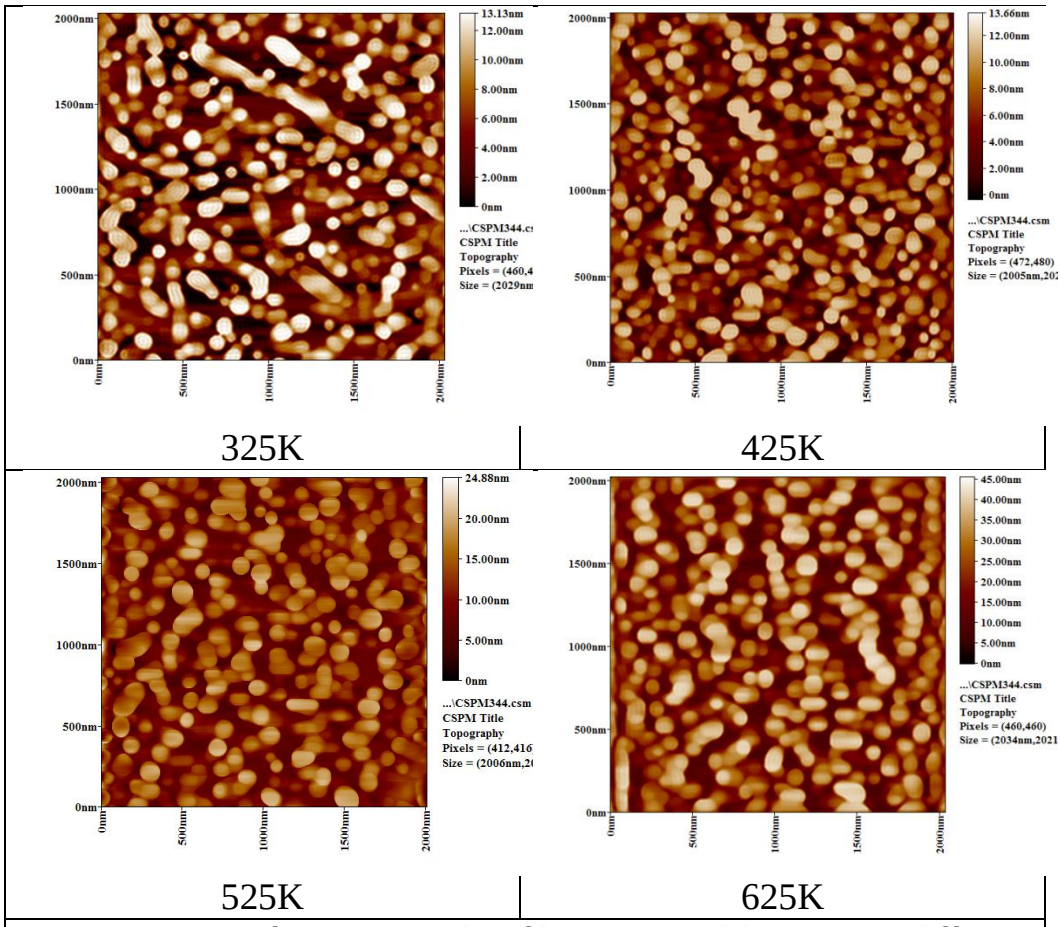


Fig.8. AFM 2D of ZnTe NPs thin films prepared by PLD at different substrate temperature (325K, 425K, 525K and 625K)

Table (2) explained the decreasing in the roughness with increase substrate temperature.

Table (2): Average grain size and roughness with increasing substarte temperature of ZnTe NPs thin films.

Substrate temperature (K)	Average grain size(nm)	Roughness (nm)
325	45.86	8.5
425	49.99	3.68
525	67.46	3.28
625	69.61	2.94

It indicates that the increase of the substarte temperature is an effective method to reduce spaces on the ZnTe thin films.

4. Optical properties

Optical transmittance spectra of ZnTe thin films deposited on glass substrate at different substrate temperatures is shown in Fig. 9.

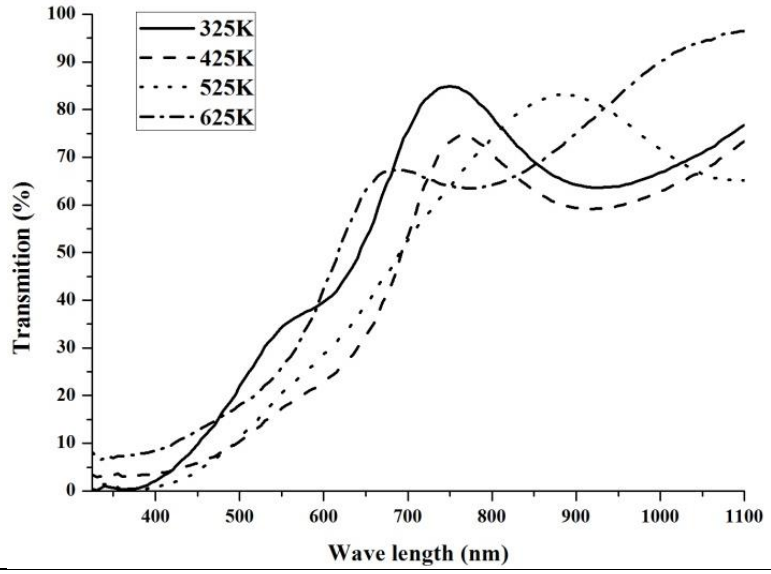


Fig.9. Transmittance spectra of ZnTe NPs thin films prepared by PLD at different substrate temperatures.

The optical transmittance of the films increases with the increase of substrate temperature from 325K to 625K. The optical band gap is calculated from eq. (4), the relationship between absorption coefficient and photon energy [33]:

$$(\boldsymbol{\alpha h\nu}) = \boldsymbol{B}\left(\boldsymbol{h\nu} - \boldsymbol{E_g}\right)^{\mathbf{1/2}} \ldots\ldots (\mathbf{4})$$

where α is the optical absorption coefficient, hν is the photon energy, E_g is the optical band gap, and B is a constant. E_g values are determined from the intercept of extrapolated linear portion of $(\alpha h\nu)^2$ versus hν curve to the photon energy axis. The shift observed at absorption edge towards lower photon energies for the increase in substrate temperature as shown in figure (10), could be attributed to the change in the grain size and the stoichiometry due to loss of Zn resulting formation of shallow acceptor levels [34].

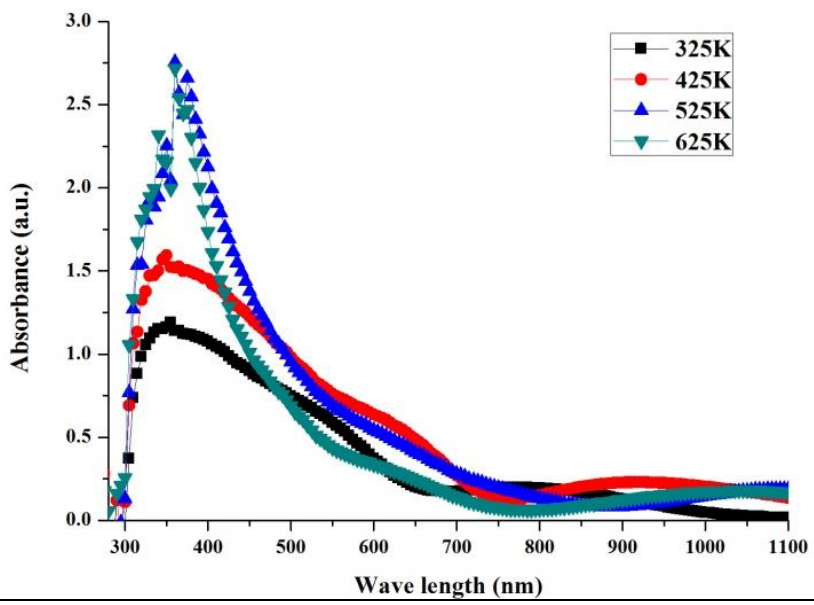


Fig.10. Optical absorbance for ZnTe NPs thin films prepared by PLD at different substrate temperatures.

The increase observed in E_g for films deposited from 325K to 625K also might be related with the variations in size and morphology of grains confirming the observation in AFM micrographs as shown in figure (11) and (12).

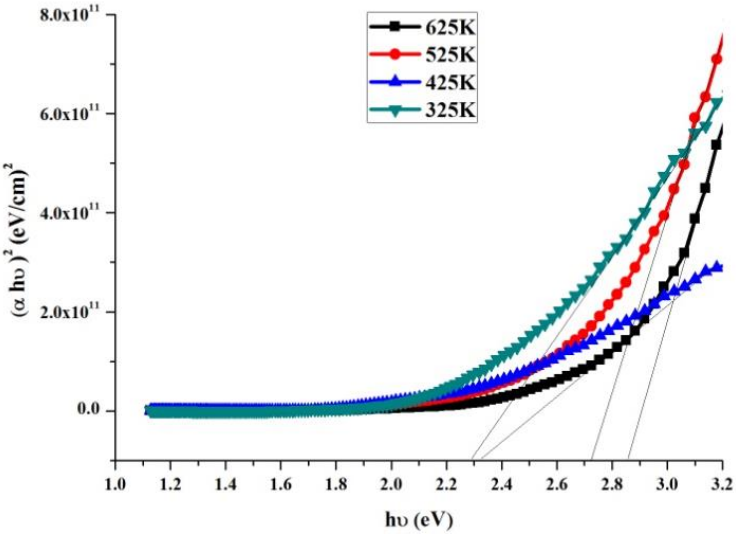


Fig.11. Variation of $(\alpha h\nu)^2$ with photon energy (hν) for ZnTe thin films prepared by PLD at different substrate temperature.

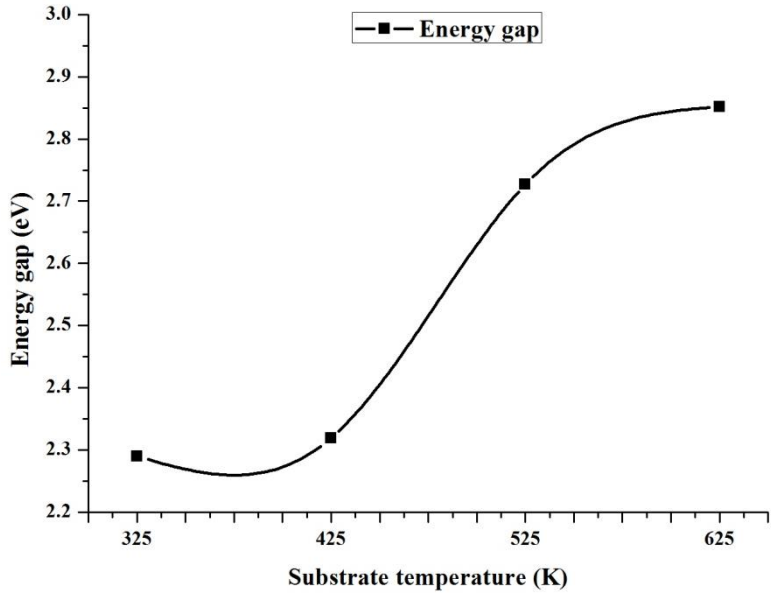


Fig.12. Energy gap varies substrate temperature for ZnTe NPs thin films prepared by PLD tecknique.

A dependence of band gap on the grain size is attributed to a quantum confinement effect related with the grain size in thin films. Similar observations have been made by some authors regarding the variation in band gap values in chalcogenide thin films [35, 36].

5. Conclosions

This research employed pulsed laser deposition technique, to prepare the ZnTe NPs thin films on glass substrates at different substrate temperatures in the range about (325, 425, 525 and 625K). X-ray diffraction patterns of ZnTe NPs thin films deposited on glass substrates showed improvement in the crystallinity of the films when increase substrate temperatures. The formation of ZnTe NPs and their spherical shape of prepared films were observed through the SEM investigations. These films were studied and the concentrations of the components were analyzed through the EDX measurements. The composition is temperature dependent, and improves with increasese deposition temperature and reached maximum at 525K. AFM images showed the increasing in the substrate temperature leads to reduction the voids of the nanoparticles in the deposited thin films ZnTe. The study of optical properties showed an increase in the value of the energy gap when increasing the substrate temperature of the prepared films. In this research we have been able to characterize and form nanoparticles using pulsed laser deposition technique on glass substrate. Laser pulse deposition technology can be an easy technique to produce optoelectronic devices by understanding the dependence of thin films properties on PLD parameters.

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