

Silver Doping Effects on ZnTe Thin Films by Thermal Evaporation Technique

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Abstract

Zinc telluride (ZnTe) thin films were fabricated by thermal evaporation method on corning glass substrates. ZnTe thin films were doped with silver (Ag) by dipping in low concentrated solution (0.2 g/200 ml) of $\text{AgNO}_3 \times \text{H}_2\text{O}$ at room temperature. X-ray diffraction technique was used to investigate the structural behavior of ZnTe samples. Optical investigations were done by using spectrophotometer. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to analyze the surface and composition of the thin film samples respectively. Electrical investigations were done by using Van Der Pauw and Hall measurement system. It was found that prepared samples showed polycrystalline structure with $\langle 111 \rangle$ as preferred orientation. Optical study showed that with increasing thickness, grain size increased but optical transmission and energy band gap were decreased. It was observed that value of resistivity of these samples decreased with increasing thickness and Ag composition. The results were compared before and after Ag doping in ZnTe thin films samples for the solar cell applications.

Keywords: ZnTe thin films; Vacuum coating; Resistivity; Energy band gap

Introduction

Zinc telluride (ZnTe) is one of the prototypes of II-VI semiconductor materials. It is grey or brownish-red powder. It exists in both 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.

It can produce green light of wavelength 550 nm, which is in the range corresponding to the maximum sensitivity of the human eye [1-5]. ZnTe has been used in γ -ray detectors, solar cells [6] switching devices [7] and optoelectronic devices [8].

ZnTe thin films can be prepared by using different methods including chemical vapor deposition and physical vapor deposition (PVD) techniques. However, deposition under vacuum has many advantages over the other techniques, because films properties can be controlled more precisely [9]. In PVD, ZnTe thin films can be fabricated by using closed space sublimation (CSS) technique [10], sputtering [11], electro-deposition process [12], electron beam evaporation [13] and also pulse laser deposition technique [14]. The CSS has an advantage of efficient utilization of material due to small distance between the source and substrate [15]. This is helpful in controlling the crystallinity of the films. In our experiment, ZnTe thin films were fabricated by thermal evaporation method on glass substrates.

Experimental Section

ZnTe thin films were fabricated by thermal evaporation method on the glass substrate of size 25 mm \times 75 mm. Substrate was cleaned for 20 min in pure IPA bath by using ultrasonic cleaner. ZnTe powder, 99.99% pure made by Aldrich (USA) company was used as source material. ZnTe powder was spread on the graphite boat which was heated by halogen lamp of 1000 W to evaporate it. Substrate was kept at a distance of 5 mm from the source. It was heated with another halogen lamp of 550 W. Two K-type thermocouples were used to measure the temperatures. Source temperature was kept at 550°C and substrate temperature was 460°C. These temperatures were controlled by using

temperature controllers. Required vacuum was obtained by using the rotary vane pump. During the formation of all ZnTe thin films, source temperature, substrate temperature and pressure inside the chamber were not varied but deposition time was changed so as to form ZnTe thin films having different thicknesses. The deposition time for ZnTe samples were (1, 4, 6, 7, 8, 12) minutes respectively. Thicknesses of the thin films were found optically by using spectrophotometer through transmission spectrum. It was found that with increasing deposition time, thickness increases.

In the next step, Ag doped ZnTe thin films were prepared by dipping as-deposited ZnTe thin films in dilute (0.20 g/200 mL) $\text{AgNO}_3 \times \text{H}_2\text{O}$ solution at room temperature for different immersion times. After that Ag doped thin films were annealed at 380°C under vacuum (10^{-3} mbr) for 1 hour to make the diffusion of Ag into the thin film samples. Here we consider the thin film whose deposition time was 4 min and doped with Ag in immersion time (5, 10, 15, 20) minutes having thickness (645, 529, 669, 680) nm.

Doped Ag samples were then characterized to make the comparison between doped and undoped samples. X-rays diffraction technique (XRD) was used to study the structure of samples. Scanning electron microscope (SEM) was used to study the microstructure and surface of the samples. To analyse the composition of Zn, Te and Ag of all the doped samples, EDX technique was used. Optical properties such as refractive index, energy band gap and absorption coefficient were

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Received September 14, 2017; **Accepted** October 16, 2017; **Published** October 26, 2017

Citation: Nazar AS, Syed AA, Murrawat A (2017) Silver Doping Effects on ZnTe Thin Films by Thermal Evaporation Technique. J Material Sci Eng 6: 388. doi: [10.4172/2169-0022.1000388](https://doi.org/10.4172/2169-0022.1000388)

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calculated by using transmission spectra of range 250 nm to 2000 nm wavelength with the help of spectrophotometer. Hall measurements were done to study the mobility and resistivity of the samples.

Results and Discussion

Structural analysis

X-ray diffraction technique was used to study the structure of as-deposited and Ag doped ZnTe thin film samples. For all samples diffraction angle varies from 20 to 60°. In bulk form ZnTe material either exists in cubic (zinc blende) or in hexagonal (wurtzite) crystal structure [16]. The type of the structure that it can show depends upon the growth conditions.

The crystal structure was found to be simple cubic with preferred orientation along (111) direction and polycrystalline in nature. The peaks of as-deposited ZnTe film shown in Figure 1 are matched with reference ASTM card number 01-072-4848. The maximum intensity peaks are related to the (111) plane of simple cubic structure. So ZnTe crystal has preferred orientation in <111> direction [17,18].

To calculate the average crystallite size L of polycrystalline thin films, Scherrer formula [19] was used given by:

$$L (\text{Å}) = k \lambda (\text{Å}) / (\beta \cos \theta)$$

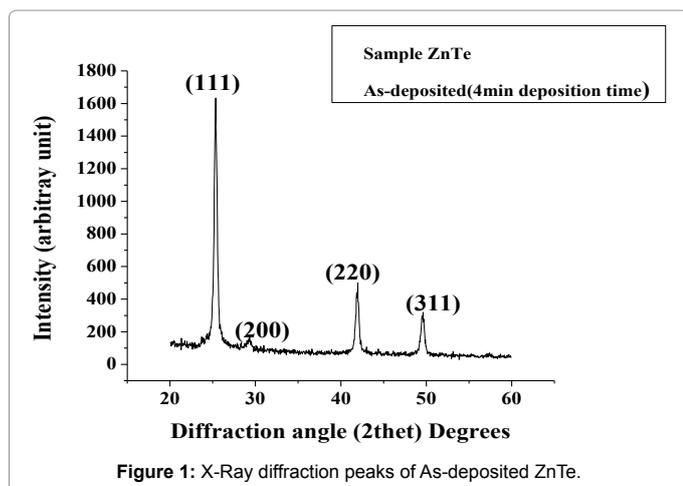
From the XRD data, dislocation density was calculated by using the formula [19].

$$\delta = 1/L^2$$

Micro strain was calculated by using the formula [19,20].

$$\text{Micro strain } (\epsilon) = (\beta \cos \theta) / 4$$

Thin films having large crystallite size show lesser dislocation density than the thin films having low crystallite size and due to large value of dislocation density peak broadening occurs, which indicates presence of defects in the samples. Table 1 shows the values of crystallite size and dislocation density of as-deposited and Ag doped (20 min) ZnTe sample.



Sample ID	Crystallite Size (Å)	Dislocation Density/cm ²
ZnTe	309	1.046E+11
ZnTe doped (20 min)	270	1.367E+11

Table 1: Values of crystallite size and dislocation density of as-deposited and Ag doped (20 min) ZnTe sample.

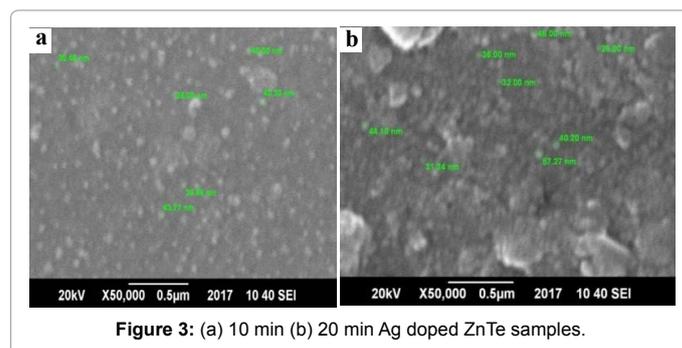
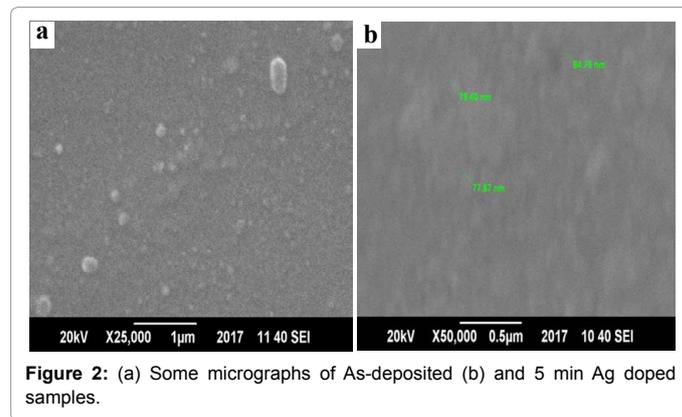
After Ag doping, an XRD spectrum of ZnTe sample (20 min immersion) was also studied. It is found that its one peak is at diffraction angle 2θ of 25.3116° and corresponds to (111) plane of cubic crystal structure. This is matched with reference card number 01-072-4848. Another peak is observed at diffraction angle 2θ of 41.8520° corresponding to (202) plane of rhombohedra of AgTe₃. This is matched with reference card number 01-076-2328. Crystallite size after doping is decreased from 309 Å to 270 Å and dislocation density is increased from value 1.04 × 10¹¹/cm² to 1.36 × 10¹¹/cm². Also value of micro strain is increased from 1.17 × 10⁻³ to 1.33 × 10⁻³ due to this variation in d-spacing (Δd) is changed from 4.131 × 10⁻³ Å to 4.721 × 10⁻³ Å as shown in Table 2.

Surface study

Scanning electron microscope was used to analyze the surface of thin film samples. This gives clear view of surface of the thin film formed on the substrate. In Figure 2 micrograph of As-deposited ZnTe sample shows that its surface is not smooth. After Ag doping for 5 min and annealing at 380°C, micrograph of ZnTe sample shows that spots or clusters have been removed and size of the grains is almost same at different locations. Also surface of this sample was found to be the smoothest surface. Figure 3 micrographs for 10 min and 20 min doping of ZnTe samples show that surfaces are rough and grain size is not uniform, at some points it is very large and at other points it is very small.

Sample ID	Micro strain (×10 ⁻³)	d (Å)	d ₀ (Å)	Δd (×10 ⁻³ Å)
ZnTe	1.172	3.519	3.523	4.131
Ag doped ZnTe (20 min)	1.339	3.518	3.523	4.721

Table 2: Values of micro strain and variation in d-spacing (Δd) due to micro strain of as-deposited and Ag doped (20 min) ZnTe sample.



Compositional analysis

Energy dispersive X-ray spectroscopy: To find the compositions of the Zn, Te and Ag atoms in the sample, energy dispersive X-ray spectroscopy (EDX) technique was used. EDX results of ZnTe doped thin film samples are shown in Figure 4.

It is found that with increasing immersion time, Ag concentration in the thin film samples increases as shown in Table 3.

Electrical properties

By using Hall measurement system (Ecopia HMS 3000) resistivity, mobility and sheet concentration of as-deposited ZnTe thin films were measured at room temperature [19]. Table 4 shows the relation between resistivity and thickness of the samples. It is found that with increasing thickness, the value of resistivity decreases. The resistivity is related to grain size or dislocation density which corresponds to presence of more defects in the sample [21,22]. A sample having low grain size or having high value of dislocation density shows high value of resistivity. On the other hand, with increasing the thickness of the sample at the given temperature and pressure, grain size increases and as a result, resistivity of the material decreases.

Mobility of the sample increases with increasing thickness. As mobility depends upon the conductivity and conductivity is inversely

Immersion time (min)	Ag Mass%
5	0.83
10	1.05
15	3.25
20	3.38

Table 3: Immersion time and Ag concentration in Ag doped ZnTe samples.

proportional to the resistivity. Table 4 shows the thickness, Resistivity mobility of the as-deposited samples.

After doping the samples for different immersion times, change in resistivity was also observed. Variation in resistivity after doping is shown in Table 5. Value of resistivity is decreased from 4.02×10^7 ohm-cm to 1.14×10^2 ohm-cm with increasing doping time. The value of resistivity could be decreased to lower value by increasing mass% of silver in ZnTe samples.

Optical properties

The optical parameters like energy band gap through these films and refractive index were determined by applying the Swanepoel model, measuring the transmission. The optical thickness d was found by the following relation.

$$d = \frac{1}{4n} \left[\frac{\lambda_m \lambda_M}{\lambda_M - \lambda_m} \right]$$

and

$$n = \frac{(M + (M^2 - 4n_s)^{1/2})^{1/2}}{2}$$

Where n_s is substrate refractive index and M is number of oscillations given by the formula:

$$M = 1 + n_s^2 + 4n_s \left(\frac{T_M - T_m}{T_M T_m} \right)$$

Where T_M and T_m are the values taken from the transmission spectra at which maxima and minima occur respectively. To calculate the thickness of a sample, values of λ_M and λ_m corresponding to T_M and T_m are found which are used to calculate thickness. To find energy band

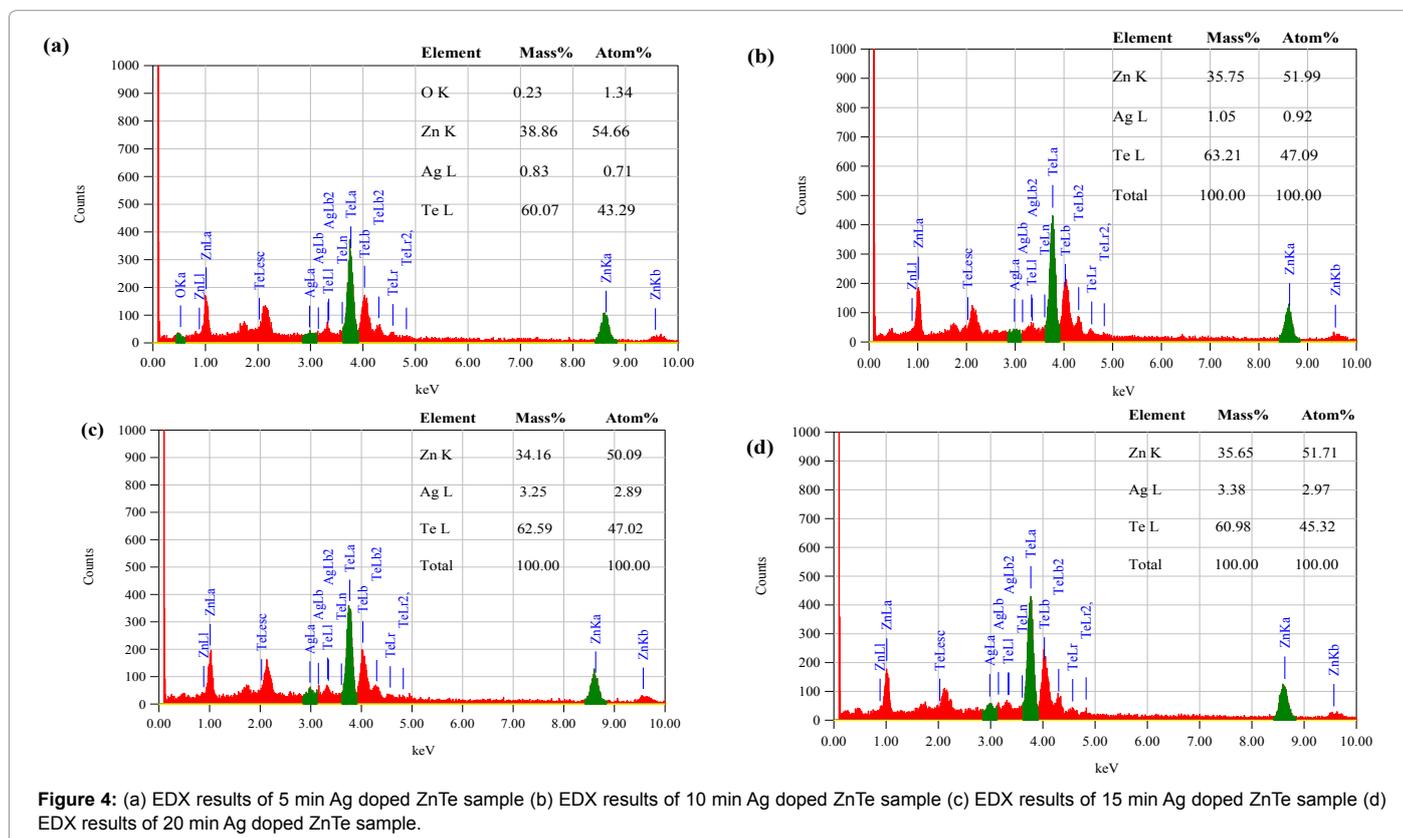


Figure 4: (a) EDX results of 5 min Ag doped ZnTe sample (b) EDX results of 10 min Ag doped ZnTe sample (c) EDX results of 15 min Ag doped ZnTe sample (d) EDX results of 20 min Ag doped ZnTe sample.

Sample ID	Deposition Time (min)	Thickness (nm)	Resistivity (ohm-cm)	Conductivity (ohm-cm) ⁻¹	Mobility (cm ² /Vs)
1	8	834	4.07E+06	2.45E-07	5.82E+02
2	7	814	9.04E+06	1.10E-07	3.50E+01
3	6	749	1.20E+07	8.33E-08	1.80E+01
4	4	627	4.02E+07	2.48E-08	8.10E+02

Table 4: Thickness, Resistivity mobility of the as-deposited samples.

Sample ID	Thickness (nm)	Resistivity (ohm-cm)	Conductivity (ohm-cm) ⁻¹
Ag doped ZnTe (min)			
5	645	9.98 × 10 ⁴	1.002 × 10 ⁻⁵
10	529	2.23 × 10 ³	4.48 × 10 ⁻⁴
15	669	9.76 × 10 ²	1.02 × 10 ⁻³
20	680	1.14 × 10 ²	8.77 × 10 ⁻³

Table 5: Values of resistivity of the Ag doped ZnTe samples.

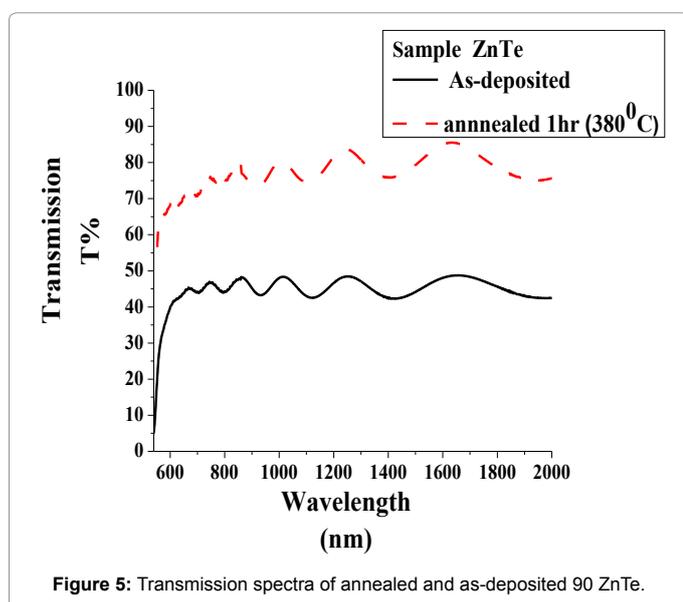


Figure 5: Transmission spectra of annealed and as-deposited 90 ZnTe.

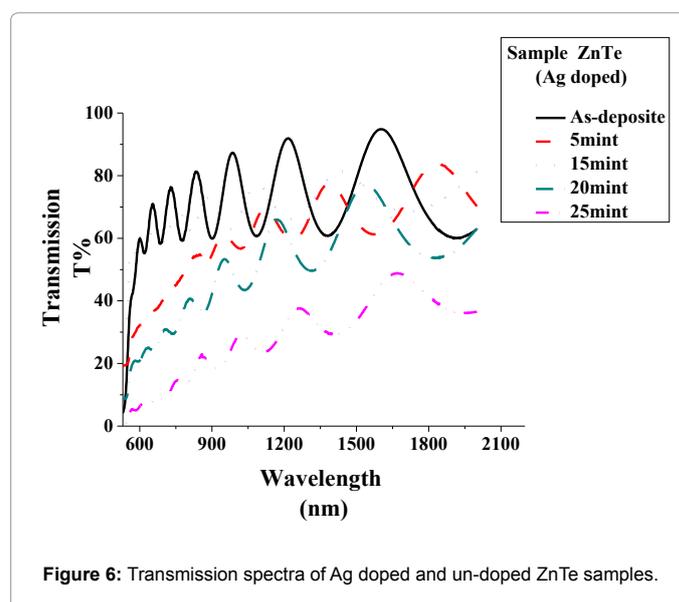


Figure 6: Transmission spectra of Ag doped and un-doped ZnTe samples.

gap, energy Vs (alpha × energy)² graph is plotted [12]. Where energy E is defined by the relation

$$E_g = hc/\lambda$$

Where 'c' is the velocity of light and 'h' is Planks constant.

The transmission curves for as-deposited and annealed at 380°C for 1 h sample ZnTe is shown in Figure 5.

The transmission spectra of Ag doped ZnTe samples are shown in Figure 6. It is found that with increasing the silver doping, transmission through the samples decreases because of reflecting properties of silver material.

On finding the thickness and refractive index of Ag doped samples, it is observed that values of refractive index decreased after doping and thickness of the sample is found to increase.

It is found from the Figure 7 that with increasing the immersion time, value of energy band gap decreases. It is observed that after annealing process the value of transmission improves from 48% (as-deposited) to 85%.

Conclusions

The experimental results show that ZnTe thin films prepared by

CSS technique have polycrystalline structure with preferred growth orientation in <111> direction. The average crystallite size increased from 216.34 Å to 240.41 Å with increasing thickness. Value of crystallite size after doping (20 min) decreases from 309 Å to 270 Å and value of micro strain increases from 1.17 × 10⁻³ to 1.33 × 10⁻³ after doping (20 min). Optical study shows that optical transmission decreases with increasing the thickness and silver mass% as dopant because silver is a good reflector. It has also been observed that with increasing the thickness, refractive index has decreased. There is also small decrease in the energy band gap from 2.229 eV to 2.217 eV with doping. On comparing the as-deposited and annealed sample, it has been found that value of optical transmission increases. The composition of silver in the sample increased from 0.83 mass% to 3.38 mass%. With annealing, surface of the thin film samples becomes better and smoother. It is also observed that as-deposited ZnTe films prepared by CSS method have high value of resistivity nearly equal to 1.2 × 10⁷ Ω-cm. The Value of resistivity decreases with increasing the film thickness. With increasing Ag composition, resistivity dropped to 1.14 × 10² Ω-cm with 3.38 mass% of Ag. The value of resistivity can be decreased further by increasing the silver ratio in ZnTe films. The important factor is to decrease the resistivity of the films but not at the cost of transmission loss so that it can be used efficiently in opto-electronic devices/solar cells.

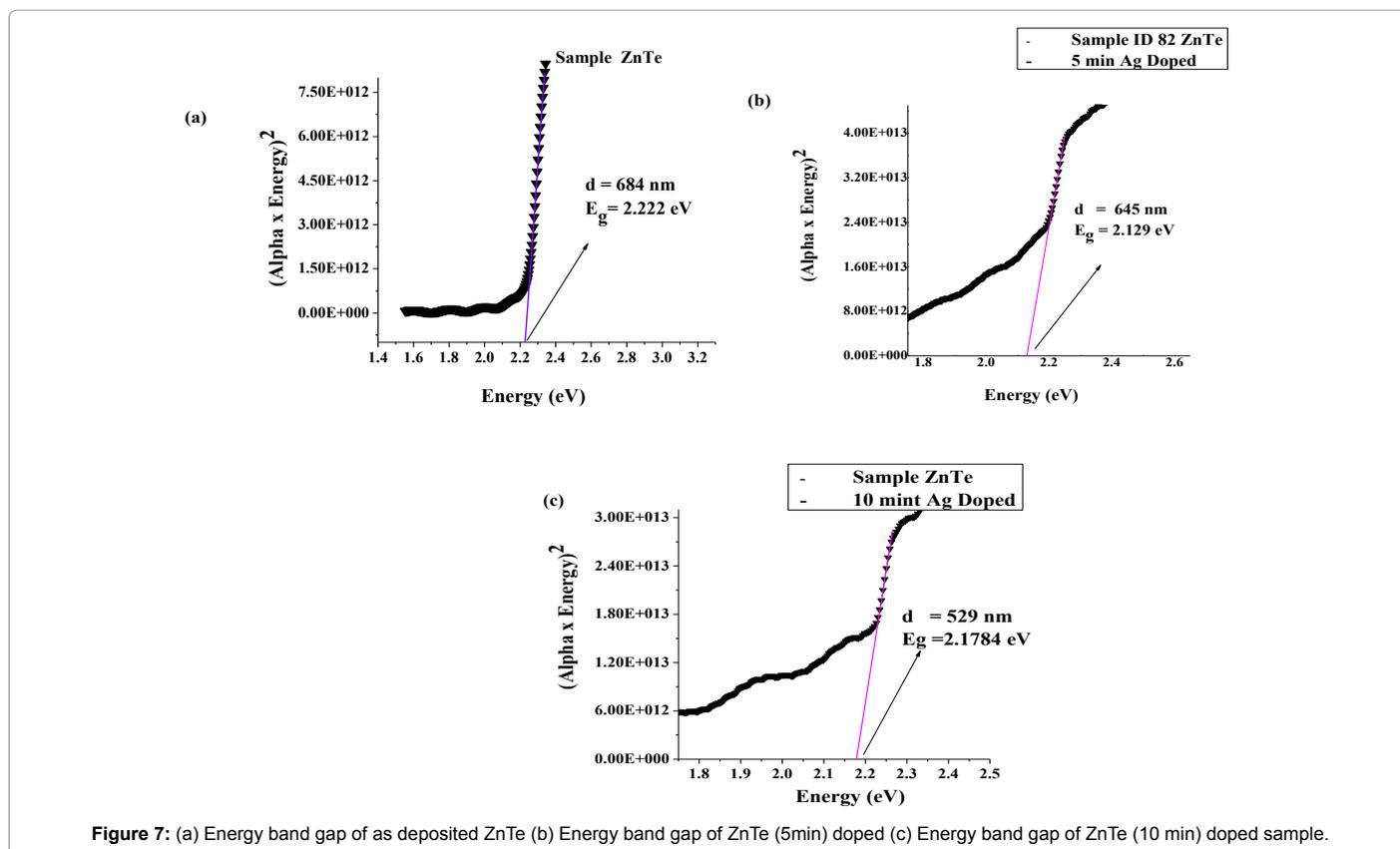


Figure 7: (a) Energy band gap of as deposited ZnTe (b) Energy band gap of ZnTe (5min) doped (c) Energy band gap of ZnTe (10 min) doped sample.

Acknowledgements

The authors are very grateful to the Higher Education Commission (HEC) of Pakistan for financial support through project # 20-1187/R&D/09 and COMSATS Institute of Information Technology (CIIT) for research project and research environment.

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