Chalcogenide Letters Vol. 7, No. 1, January 2010, p. 21 - 29

STRUCTURAL, ELEMENTAL COMPOSITIONS AND OPTICAL PROPERTIES OF ZnTe:V THIN FILMS

M. S. HOSSAIN[a*], R. ISLAM[b], K. A. KHAN[b]
[a]*Department of Physics, Rajshahi University of Engineering & Technology, Rajshahi-6204, Bangladesh*
[b]*Department of Applied Physics and Electronic Engineering, University of Rajshahi, Rajshahi-6205, Bangladesh*

Vanadium doped zinc telluride (ZnTe:V) thin films of various thicknesses for a particular composition of 2.5wt% V were deposited onto glass substrates by e-beam evaporation technique in vacuum at a pressure of 8×10^{-4} Pa. The deposition rate of the ZnTe:V films was maintained at 2.05 nms^{-1}. The optical properties of ZnTe:V thin films for different film thicknesses have been studied in detail. Structural study of the films was performed by x-ray diffraction technique and it was found that the films are mixed crystalline in nature. Surface morphological study was done by using SEM technique. EDAX method was also used to determine the elemental composition in deposited thin films. The optical properties of as-deposited and annealed ZnTe:V films for different thicknesses were studied in the wavelength range $300 < \lambda < 2500$ nm, respectively. For both types of samples, the values of the Urbach tail energy, optical band gap, refractive index, extinction coefficient and real part of dielectric constants were evaluated for different film thicknesses, respectively. Evaluation of these parameters may help in view of their technological applications in selective surface as well as in optoelectronic devices.

(Received December 22, 2009; accepted January 14, 2010)

Keywords: ZnTe:V thin film, E-beam evaporation technique, Surface morphology, Urbach tail energy, Optical band gap, Refractive index

1. Introduction

ZnTe is a low cost semiconducting material of the II-VI family. This crystal is usually a cubic, zincblende type in structure with lattice constant a_o = 6.1034 Å. Like most of the ZnTe crystals is normally a semiconductor. In thin film, it is more insulating than the bulk. Usually, it is a material of high absorption coefficient [1] and shows a p-type [2, 3] in nature. ZnTe has direct [1, 4] transition of wide band gap [1] of 1.7 to 2.4 eV at room temperature. ZnTe has recently been focused of great interest due its low cost, wide band gap and high absorption co-efficient for application to photovoltaic [5] and photoelectrochemical cells [6-9]. It is a promising compound for development of various solid state devices including the blue light emitting diodes [10, 11], laser diodes [12], solar cells [10-12], microwave devices [13] and various optoelectronic devices [14-16].

Literature reports [17, 18] indicate that the ZnTe exhibits improved photorefractive response when it is doped with vanadium. Vanadium is believed to be a suitable impurity in ZnTe and it has attractive use in a variety of applications including optical power limiting, optical computing and optical communication [18]. Since optical response is of great importance for many device applications, many efforts have been made to obtain optical response. Although there have been a number of investigations on the ZnTe films by a number of researchers, no systematic study appears to have been done on the structural and optical properties of ZnTe thin films in particular

*Corresponding author: sazzad_phy@yahoo.com

using vanadium as a dopant. Hence, there is a need to systematic study, on structural and optical properties of vanadium doped zinc telluride (ZnTe:V) thin films deposited by e-beam technique. In this paper, we present and discussed on the structural and optical properties of e-beam deposited ZnTe:V thin films in view of their applications in optoelectronic devices.

2. Experimental

ZnTe:V thin films have been deposited onto glass substrate from the mixture of ZnTe powder (99.999% pure) and vanadium powder (99.999% pure) obtained from Aldrich Chemical Company, USA using electron bombardment heating technique in vacuum at a pressure of ~8×10^{-4} Pa. The films of different thicknesses for a particular composition of 2.5wt% V were deposited onto glass substrate at room temperature. One mask was used for the deposition of the samples. The deposition rate of all films was maintained at 2.05 nms^{-1}. The substrate-holder was at about 0.09 m above the source material. A mechanical shutter was operated from outside, isolated the substrate from the evaporant.

The deposition chamber was thoroughly cleaned with emery paper and cotton wool by wetting acetone and was then dried with a dryer (model: HP4514). A small quantity of source material was loaded into clean cermet-hearth based on the source turret. Cleaned substrate was placed on the substrate-holder and the chamber bell jar was then placed on the base plate. When the chamber pressure reduced to 8×10^{-4} Pa, deposition was then started with beam current 40-50 mA by turning on the low-tension control switch of electron beam power supply (EBS) unit. Details of the film deposition process were reported by author's work [19]. After completing the deposition, taking them out from the vacuum chamber, the film thickness was determined by the Tolansky interference method [20] with an accuracy of ±5 nm.

ZnTe:V thin films are annealed by a specially designed heater. A flat nichrome wire strip heater covered with mica sheet has been used to heat the film devices. In the heating cycle, the temperature of the film is increased to 473 K, held there for 3 hours and then it is cooled in air. This annealing procedure is maintained for all annealed films. The temperature is measured by a digital thermometer (England, model: Stk.610-067) with chromel-alumel thermocouple placed on the middle of the substrate. The heating and cooling rate is kept at about 10 K/min for each sample.

The structural, surface micrographs, elemental composition and spectral measurements of ZnTe:V thin films of thickness 100 to 250 nm for both as-deposited and annealed films were done by using x-ray diffraction (XRD) technique, scanning electron microscopy (SEM), energy dispersive analysis of x-ray (EDAX) method and double beam spectrophotometer, respectively.

3. Results and discussion

3.1. Structural study

The structure of as-deposited and annealed ZnTe:V thin films of different thicknesses for a particular composition of 2.5wt% V were examined by x-ray diffraction (XRD) technique with the monochromatic Cu-Kα radiation using an apparatus, RINT 2200, Rigaku, Japan. Peak intensities were recorded corresponding to 2θ values. Figs. 1(a) and (b) illustrate the XRD spectra of a 150 nm thick as-deposited and annealed ZnTe:V thin films of composition 2.5wt% V onto glass substrate, respectively. In Fig. 1(a) of as-deposited ZnTe:V films, three peaks are observed at 2θ values of 34.16°, 39.26° and 42.85°, respectively. These peaks correspond to the phases with plane V_6O_{11} (022), Zn (100) and $ZnTeO_3$ (124), respectively. These phases and planes are found from the JCPDS cards [21, 22, 23], respectively. For annealed ZnTe:V film of Fig. 1(b), four peaks are observed at 2θ values of 31.67°, 34.37°, 36.26° and 41.69°, which correspond to V_4O_9 (410), V_2O_5 (310), Zn (002) and ZnTe (220) phases with plane, respectively. These phases and planes are also found from the JCPDS cards [24, 25, 22, 26], respectively.

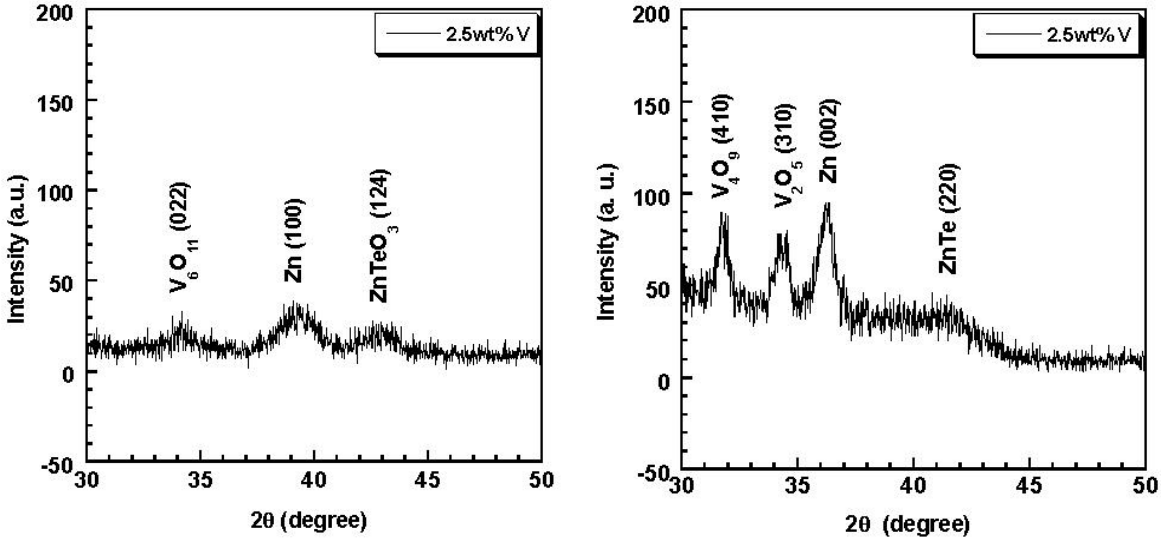

Fig. 1. XRD spectra for a 150 nm thick (a) as-deposited and (b) annealed ZnTe:V thin films of composition 2.5wt% V.

In annealed condition, the XRD peaks show up more prominently than that of as-deposited one. This could be attributed to the more crystalline nature of the annealed films. Moreover, the XRD study shows a number of oxide phases present in the author's samples. This oxide phases are formed after deposition by oxygen particles absorbed from the environment replacing one or two of the host elements in ZnTe:V. So, examination of both as-deposited as well as annealed ZnTe:V thin films exhibit the structure of the sample is of a mixed crystalline in nature.

3.2. Surface morphology study

The surface morphology of the as-deposited as well as annealed ZnTe:V thin films of various thicknesses were observed by scanning electron microscopy (SEM) using Philips, Model: XL-30, operated at accelerating 10 KV potential. Figs. 2 (a) and (b) show the SEM micrographs of surface morphology for a 100 nm thick as-deposited and annealed ZnTe:V thin films of composition 2.5wt% V, respectively. From both the micrographs, it shows that the film surfaces are dense and compact in nature. In the case of as-deposited ZnTe:V thin film, a few numbers of small-size-dots or pits were observed distributed randomly over the whole sample. After annealing, the dots or pits were removed and a very smooth surface morphology was obtained. From the study of as-deposited as in Fig. 2(a) and annealed as in Fig. 2(b) films, it is concluded that the film surfaces are dense, smooth and have a compact in nature. Due to the limitation of available SEM system, it was not possible to capture high magnification images of our samples.

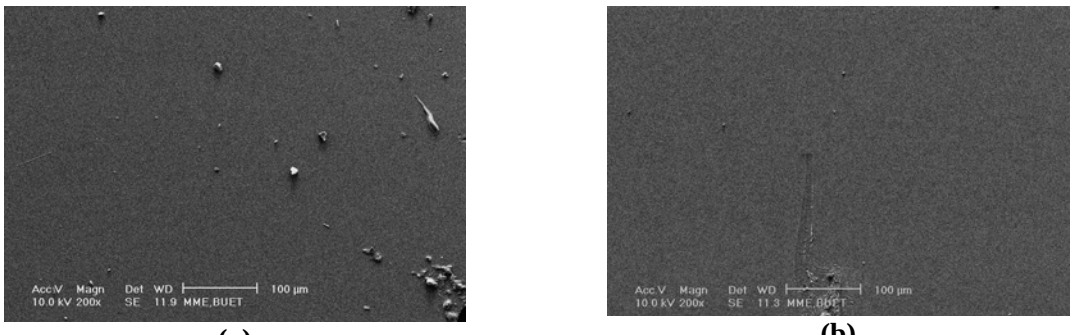

Fig. 2. SEM micrographs of 100 nm thick (a) as-deposited and (b) annealed ZnTe:V thin film of composition 2.5wt% V.

3.3. Elemental composition study

The analysis of the chemical compositions for the as-deposited as well as annealed ZnTe:V thin films of thickness 100 nm was estimated by using the method of energy dispersive analysis of x-ray (EDAX). The results of elemental compositions are shown in Table 1. It is seen from Table 1 that for a 100 nm thick as-deposited and annealed ZnTe:V samples, the elemental composition of V and Zn do increase in annealed case compared to that of as-deposited one whereas, the Te composition is seen to decrease in annealed case. So, the EDAX study suggests that author's ZnTe:V samples are non-stoichiometric in nature.

Table 1. Estimated elemental compositions of V, Zn and Te by EDAX method.

Thickness nm	Composition wt% V	EDAX results			Remarks
		V (wt%)	Zn (wt%)	Te (wt%)	
100	2.5	02.63(±0.51)	41.98(±0.59)	55.39(±1.02)	As-deposited
100	2.5	03.55(±0.41)	42.45(±0.43)	54.00(±1.07)	Annealed

3.4. Optical study

To measure the optical properties of ZnTe:V thin films for different thicknesses of a particular composition 2.5wt% V deposited onto glass substrate, Perkin-Elmer lamda-19, (UV/VIS/NIR), double beam spectrophotometer was used. For each sample of different thicknesses, transmittance and reflectance spectra were measured as a function of wavelength in the $300<\lambda<2500$ nm ranges, respectively.

Fig. 3(a) shows the transmittance spectra of as-deposited ZnTe:V thin films as a function of wavelength for 100, 150, 200 and 250 nm thicknesses, respectively. From this figure it is observed that the transmittance value decreases with the increase of film thickness for all investigated samples. This behavior is well agreed with the report of other worker [27]. From this figure, it is also found that the transmittance value of thick 250 nm sample shows anomaly in near infrared region from 1351.11 to 1711.67 nm, respectively. For each sample of ZnTe:V thin films, the reflectance data were measured as a function of wavelength. Fig. 3(b) shows the reflectance spectra of as-deposited ZnTe:V thin films for different thicknesses of a vanadium composition 2.5wt% V as a function of wavelength in the range $300 < \lambda < 800$ nm. All reflectance spectra of the samples of this figure show the interference in nature in visible and near infrared region.

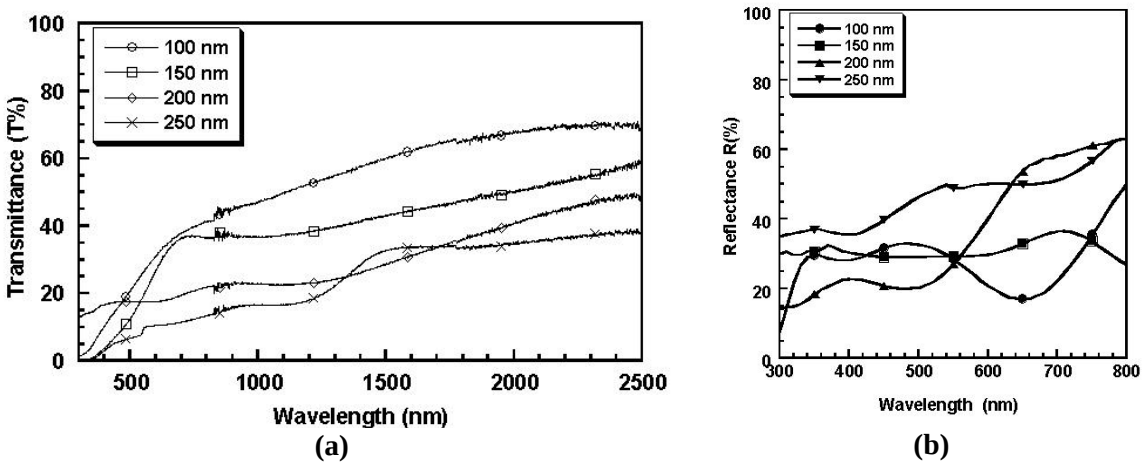

Fig. 3. (a) Transmittance and (b) reflectance spectra of as-deposited ZnTe:V thin films of composition 2.5wt% V for 100, 150, 200 and 250 nm thicknesses, respectively.

The absorption coefficients α of the ZnTe:V thin films of a composition 2.5wt% V for different thicknesses were calculated from the measured transmittance and reflectance data using the following relation as Pankove [28].

$$\alpha = \frac{1}{t}\ln\left[\frac{1-R^2}{T}\right] \quad (1)$$

where T is the transmittance, R is the reflectance, $k_o = (\alpha\lambda/4\pi)$ is the extinction coefficient, λ is the wavelength used and t is the thickness of t he films. The absorption coefficients as a function of photon energy (hν) are plotted of the ZnTe:V thin films for different thicknesses and they are shown in Fig. 4. From this figure, it is seen that the absorption values of α increase in the region of $1.55 \leq h\nu \leq 2.0$ eV and then it continues to increasing until it reaches around the absorption value of 2.78×10^7 m^{-1} at 3.44 eV.

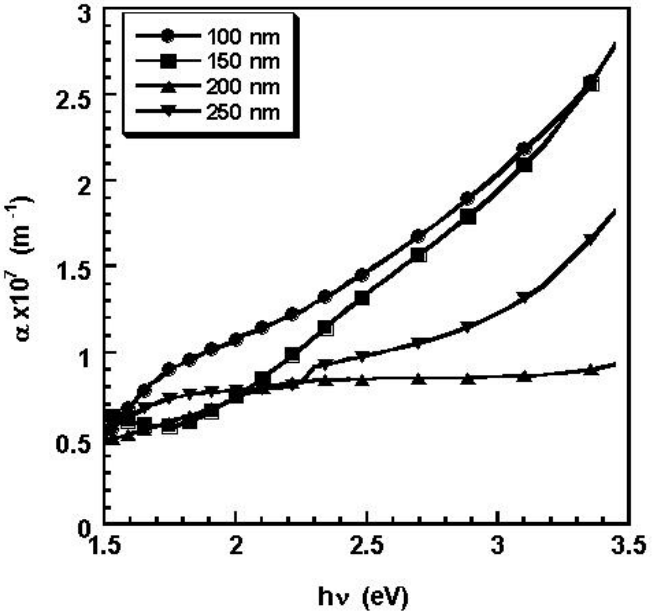

Fig. 4. Absorption coefficient (α) vs. photon energy (hν) of as-deposited ZnTe:V films for different thicknesses at a composition of 2.5wt% V.

According to Tauc [29], absorption spectrum is possible to separate three distinct regions of amorphous as well as crystalline semiconductors. The first is weak absorption tail, which originates from defects and impurities; the second is the exponential edge region, which is strongly related to the structural randomness of the system and the third is the high absorption region that determines the optical band gap. Below 1.70 eV of the weak absorption tail, the absorption coefficient α indicates a long band tail in the absorption curves, which may cause due to defects and impurities of the samples [30].

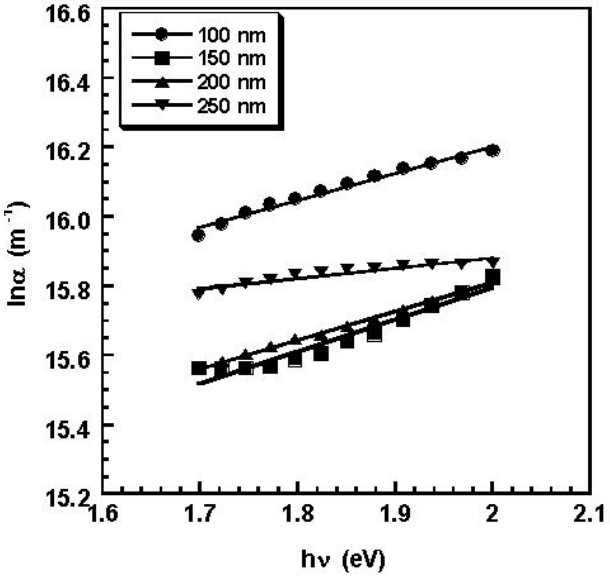

Fig. 5. Plot of lnα vs. hν for different thicknesses of as-deposited ZnTe:V thin films at a composition of 2.5wt% V.

In the exponent edge (from 1.70 to 2.0 eV), the values of absorption coefficient α for ZnTe:V thin films lie in the absorption regions of $0.56\times10^7 < \alpha < 2.36\times10^7$ m^{-1}. In this range, the absorption coefficient is governed by the following relation as Urbach law [31],

$$\alpha = \alpha_0 \exp(h\nu / E_e) \tag{2}$$

where α_o is a constant, hν is incident photon energy and E_e is the width of band tail or Urbach tail energy. Using Eq. 2, the obtained data of lnα is plotted as a function of photon energy (hν) for different film thicknesses which are shown in Fig. 5. From the slope of these curves, the calculated values of E_e for different film thicknesses are tabulated in Table 2, respectively.

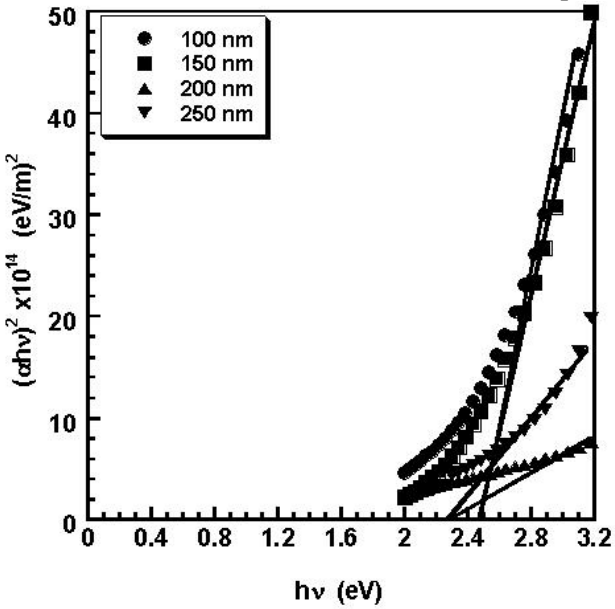

Fig. 6. Plot of $(\alpha h\nu)^2$ vs. hν for ZnTe:V films of different thicknesses at a particular composition of 2.5wt% V.

In the high absorption region (>2.0 eV), α can be represented by the relation as Pankove [28],

$$\alpha h\nu = B(h\nu - E_g)^P \quad (3)$$

where B is constant depending on the transition probability, E_g is the optical band gap and P is an index that characterizes the optical absorption process and is theoretically equal to 2, 1/2, 3 or 3/2 for indirect allowed [32], direct allowed [1], indirect forbidden and direct forbidden transitions, respectively. The usual method for determining the value of the band gap E_g involves with the plotting a graph of $(\alpha h\nu)^{1/P}$ versus photon energy ($h\nu$) in accordance to Eq. 3. If an appropriate value of P is used to obtain a linear plot, the value of E_g will be given by the intercept on the $h\nu$ axis. To apply this relation for author's sample under investigation, a number of curves based on, $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/3}$ and $(\alpha h\nu)^{2/3}$ as a function of $h\nu$ are plotted (not shown) and it is seen from all the plots that the best fit plot is the plot of $(\alpha h\nu)^2$- $h\nu$ which covers the widest range of data. The best fit plots $(\alpha h\nu)^2$ vs. $h\nu$ of ZnTe:V samples for different thicknesses are shown in Fig. 7. Similarly, all optical parameters are evaluated of annealed ZnTe:V thin films (not shown) for different film thicknesses. The band gaps E_g obtained by extrapolating the curves to $(\alpha h\nu)^2 = 0$ for direct allowed transition and their values for the samples of different thicknesses are ranged of 1.92 to 2.49 eV, respectively. The corresponding calculated values of constant B (using Eq. 3) lie in the range of 0.30×10^8 to 1.10×10^8 m^{-1}-$eV^{1/2}$ and they are also tabulated in Table 2. The author's result of E_g for ZnTe:V sample does agree well with that of ZnTe value reported by the Rusu et al. [1].

To calculate the refractive index n and extinction coefficient k_o, the method suggested by Manifacier et al. [33, 34] is used. The refractive indices are calculated using Manifacier's formula by using the iterative method and the same iterative method is used for ZnTe thin film by Amutha et al. as [27].

$$T = \frac{16\, n_a\, n_g\, n^2 \exp(-\alpha t)}{R_1^2 + R_2^2 \exp(-2\alpha t) + 2\, R_1 R_2 \exp(-\alpha t)\cos\left(\frac{4\pi n t}{\lambda}\right)} \quad (4)$$

where $R_1 = (n + n_a)(n_g + 1)$, $R_2 = (n - n_a)(n_g - 1)$ are the absorption coefficients, n, n_a, n_g are the refractive indices of the film, air and glass substrate, respectively. The real part of dielectric constants ε_1 of ZnTe:V films were calculated using the formula $\varepsilon_1 = n^2 - k_o^2$ for different thicknesses at a particular composition of 2.5wt% V.

Table 2. Evaluated optical parameters of ZnTe:V thin films of composition 2.5wt% V for different thicknesses.

Thicknesses (nm)	As-deposited thin films						Annealed thin films					
	E_e (eV)	E_g (eV)	$B\times10^8$ ($m^{-1}eV^{1/2}$)	n	k_o	ε_1	E_e (eV)	E_g (eV)	$B\times10^8$ ($m^{-1}eV^{1/2}$)	n	k_o	ε_1
100	1.29	2.49	0.85	2.98	0.58	8.54	1.63	2.33	0.88	3.07	0.68	8.96
150	0.82	2.48	0.81	2.94	0.53	8.36	1.04	2.26	1.10	3.00	1.06	7.88
200	1.17	2.29	0.30	2.92	0.34	8.41	1.15	2.20	0.87	2.96	0.86	8.02
250	2.14	2.27	0.44	2.89	0.39	8.20	2.01	1.92	0.54	2.93	0.72	8.07

Table 2 shows the evaluated values of optical parameters of as-deposited as well as annealed ZnTe:V thin films for different thicknesses at a composition of 2.5wt% V. It is seen from the table that the values of band gap, E_g refractive index, n and constant, B decrease with increasing film thickness in both as-deposited and annealed films. It is also found that the Urbach tail energy, E_e and extinction coefficient, k_o (calculated at wavelength 500 nm) are found to vary disproportionately with film thickness. The real part of optical dielectric constant, ε_1 is seen to decrease disproportionately in both the as-deposited and annealed films with increasing film thicknesses. Author's results of refractive index of ZnTe:V thin films ranges from 2.89 to 3.07 and their results do agree well with the value reported by Ziari et al. [17] and Shing [5], respectively.

Corresponding values of band gap energy decreases in annealed case compared to the as-deposited ones and the decreasing is seen with increasing thicknesses. It may be due to the density of the localized states increases with increasing film thicknesses and annealing of the films.

4. Conclusions

ZnTe:V thin films of different thicknesses for elemental composition 2.5wt% V have been prepared onto glass substrate at a pressure of ~8×10^{-4} Pa by e-beam evaporation technique. The deposition rate of ZnTe:V films was 2.05 nms^{-1}. X-ray diffraction study indicates that the ZnTe:V films are mixed crystalline in structure. The film surface was found dense, smooth and compact in nature by using SEM technique. EDAX method suggests that the elemental compositions of the author's samples are non-stoichiometric. The optical parameters of both the as-deposited and annealed ZnTe:V films such as, the Urbach tail energy, optical band gap, refractive index, extinction coefficient and real part of optical dielectric constant were evaluated for different film thicknesses, respectively. Evaluation of these parameters may help in view of their technological applications in selective surface as well as in optoelectronic devices

Acknowledgements

Authors gratefully acknowledge the assistance in measuring the XRD and optical data by Dr. M. Shahjahan in Japan. One of the author's M. S. Hossain is indebted to Rajshahi University of Engineering & Technology, Bangladesh for providing the study leave during this work.

References

[1] G. I. Rusu, P. Prepelita, N. Apetroaei, G. Popa, J. Optoelectron. Adv. Mater. **7**, 829 (2005).
[2] M. Aven, J. Appl. Phys. **38**, 4421 (1967).
[3] M. Aven, B. Segall, Phys. Rev. **130**, 81 (1963).
[4] A. S. Arico, Advanced Performance Materials, **4**, 115 (1997).
[5] J. Singh, Physics of Semiconductors and Their Heterostructures (McGraw-Hill, New York, 1993).
[6] A. Z. Nozik, R. Memming, J. Phys. Chem. **100**, 13061 (1996).
[7] J. O. M. Bockris, K. Uosaki, J. Electrochem. Soc. **124**, 1348 (1997).
[8] K K. Mishra, K. Rajeshwar, J. Electrochem. Soc. **273**, 169 (1978).
[9] D. Ham, K. K. Mishra, K. Rajeshwar, J. Electrochem. Soc. **138**, 100 (1991).
[10] P. V. Mayers, Proc. of 7th Commision Europian Communities Conference on Photovoltaic Solar Energy, Reidel, Dordrecht. 1121 (1986).
[11] M. Jain (ed), II-VI Semiconductor Compounds (World Scientific, Singapore, 1993).
[12] R. Bhargava (ed), Properties of Wide Bandgap II-VI Semiconductors (Inspec., London, 1997).
[13] Q. Wu, M. Litz, X. C. Zang, Appl. Phys. Lett. **68**, 2924 (1996).
[14] K. Yoshino, A. Memon, M. Yoneta, K. Ohmori, H. Saito, M. Ohishi, Phys. Status Solidi B, **229**, 977 (2002).
[15] K. Sato, M. Hanafuza, A. Noda, A. Arakawa, M. Uchida, T Asahi, O. Oda, J. Cryst. Growth, **214/215**, 1080 (2000).
[16] M. Schall, M. Walther, P. Uhd Jepsen, Phys. Rev. **B64**, 94301 (2001).
[17] M. Ziari, W. H. Steier, P. M. Ranon, Appl. Phys. Lett. **60**, 1052 (1992).
[18] J. Kreissl, K. Irmscher, Phys. Rev. **B53**, 1917 (1996).
[19] M. S. Hossain, R. Islam, K.A. Khan, Renewable Energy, **33**, 642 (2008).
[20] S. Tolansky, Multiple Beam Interferometry of Surfaces and Films (Oxford Univ. Press, London, 1948).
[21] Andersson, Jahnberg, Arkiv Kemi, JCPDS Card No.18-1451, **21**, 413 (1964).

[22] Swansun, Tatge, DC Fel, JCPDS Card No. 4-0831 (Reports, 1951).
[23] Frank-Kamenetsky, Univ. of Leningrad, USSR, Saturiwiss, JCPDS Card No. 20-1270, **54**, 199 (1967).
[24] W. Karl-Axel, W. Kjell, Acta Chem. Scan., JCPDS Card No.24-1391, **24**, 3409 (1970).
[25] Nat. Bur., Standards CIRC, JCPDS Card No.9-387, **8**, 66 (1958).
[26] Nat. Bur., Stds. U.S. Mono., JCPDS Card No.15-746, **25**, 58 (1964).
[27] R. Amutha, A. Subbarayan, R. Sathyamoorthy, Cryst. Res. Technol. **41**, 1174 (2006).
[28] J. I. Pankove, Optical Processes in Semiconductors (Prentice-Hall, New Jersey, 1971).
[29] J. Tauc, Amorphous and Liquid Semiconductors (Plenum Press, New York, 1974).
[30] A. F. Qasrawi, Cryst. Res. Technol. **40**, 610 (2005).
[31] F. Urbach, Phys. Rev. **92**, 1324 (1953).
[32] A. V. Savitskii, M. V. Kurik, K. D. Tovstyuk, Opt. Spectrose. **19**, 56 (1964).
[33] J. C. Manifacier, J. Gasiot, J. P. Fillard, J. Phys. E: Sci. Instrum. **9**, 1002 (1976).
[34] J. C. Manifacier, M. de Murcia, J. P. Fillard, E. Vicario, Thin Solid Films, **41**, 127 (1977).