

Electrical, optical properties and electronic band structure of ZnTe:V thin films

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Abstract: Vanadium doped zinc telluride thin films (ZnTe:V) of various vanadium compositions were prepared onto glass substrate by e-beam evaporation technique in vacuum at 8×10^{-4} Pa. The deposition rate of the films was maintained at 2.052 nms^{-1} . Prepared thin films were examined by x-ray diffraction technique and the film structures were exhibited mixed crystalline in nature. Electrical and optical properties of ZnTe:V thin films were studied in detail for various vanadium compositions. Temperature dependence of electrical conductivity shows a semiconducting behavior with a spectrum of activation energy. Dopant vanadium concentration increases the conductivity of the samples. The composition dependence of the activation energies were studied in the 300-413 K temperature range. Electrical conduction of ZnTe:V thin films obey the thermally activated conduction mechanism. Different optical parameters of ZnTe:V thin films were investigated for various vanadium compositions. Electronic band structure of ZnTe:V thin film is estimated using these electrical and optical properties.

Keywords: ZnTe:V thin films, E-beam technique, Activation energy, Electrical conductivity, Optical parameters, Electronic band structure

I. Introduction

Semiconductor materials of II-VI family attract attention of many scientific and industrial research groups throughout the world. Recently, zinc telluride (ZnTe) semiconductor of this family has been a focus of growing interest due to its low cost and high absorption co-efficient for potential application to photovoltaic [1,2] and photo-electrochemical [3-6] cells. ZnTe is a direct band gap of 2.2 to 2.3 eV at room temperature and usually a p-type semiconductor [7-9]. Literature [10] reports indicate that ZnTe exhibits improved photorefractive response when it is doped with vanadium. Vanadium is believed to be a deep donor in ZnTe and its theoretical studies suggest that it plays significant role in both ZnTe and CdTe where it appears in a divalent state and occupies a cation site [11,12]. It has attractive use in a variety of applications, including optical power limiting, holographic interferometry, optical computing and optical communications [10,11].

Although there have been a number of investigations on the electrical [13-15], optical [8,9,16,17], electro-optical [18-20] and switching [21-23] properties of ZnTe as well as of ZnTe:V [10-12] films by a number of researchers, but no systematic study appears to have been done on the electrical, optical properties, in particular, on electronic band structure of ZnTe:V thin films at varying deposition conditions. Hence, there is a need to systematic study on electronic band structure by comparing electrical and optical properties to assess its usefulness in a variety of photosensitive operation in optoelectronic devices. In this paper, we present and discuss the preparation, electrical, optical properties and electronic band structure of ZnTe:V thin films.

II. Experimental

Vanadium doped Zinc Telluride (ZnTe:V) thin films have been produced onto glass substrates by electron beam bombardment technique in vacuum at $\sim 8 \times 10^{-4}$ Pa from a mixture of ZnTe powder (99.999% pure) and vanadium powder (99.999% pure), obtained from Aldrich Chemical Company, USA. ZnTe:V thin films containing 2.5 to 10wt% V were of thickness 100 to 200 nm, respectively. The deposition rate of film was 2.052 nms^{-1} . Each material was weighted by an electrical balance (Mettler TOLEDO, AB 204) having a resolution of $\pm 0.0001 \text{ g}$, according to percentage composition to be used. The percentage composition of starting materials in the evaporant mixture, was determined as Khan [24],

$$\text{Weight \% V} = \frac{W_V}{W_V + W_{\text{ZnTe}}} \times 100\% \quad (1)$$

where W_V and W_{ZnTe} are the weights of vanadium (V) and zinc telluride (ZnTe), respectively. When the chamber pressure reduced to 8×10^{-4} Pa, deposition was then started with beam current of 40-50 mA by turning on the low-tension control switch. All the films were deposited at room temperature. Annealing was performed at a temperature of 473 K for duration of 3 hours. The film thickness was measured by the Tolansky interference method [25] with an accuracy of $\pm 5 \text{ nm}$.

The structure of ZnTe:V thin films of different compositions were examined by x-ray diffraction (XRD) technique using the monochromatic CuK α radiations made by an apparatus, RINT 2200, Rigaku, Japan. Examination shows that the structure of the film is mixed crystalline in nature.

I-V characteristics of ZnTe:V thin film was measured as a function of temperature in the 300 to 413 K ranges. A dc power supply (Heathkit, Model: IP-2717A) was used to pass a constant dc current through the test sample. An electrometer (Keithley, Model: 614) monitored the current through the sample and a digital multimeter (Model: DM-206) was used to measure the potential differences across each sample. Digital multimeter (Model: DL-711) was also used to measure the current.

The optical spectra of ZnTe:V thin films were measured using Perkin-Elmer lamda-19, (UV/VIS/NIR) double beam spectrophotometer as a function of wavelength.

III. Results And Discussion

3.1 Electrical conductivity

Electrical conductivity (σ) of ZnTe:V thin films are measured as a function of temperature in the 300 to 413 K ranges. The glass substrate is heated by a specially designed heater and the temperature is measured by a chromel-alumel thermocouple placed on the middle of the substrate. The conductivity is obtained by applying a dc 15 V bias across the film and recording the current and voltage simultaneously. Figure 1 shows $\ln \sigma$ vs. $1/T$ curves for compositions 2.5, 5.0, 7.5 and 10wt% V of a 150 nm thick ZnTe:V films, respectively. From the figure, it is interesting to note that conductivity appears to vary continuously with inverse temperature suggesting a thermally activated conduction mechanism. The conductivity (σ) of these samples cannot be represented by one single exponential of the form as [26],

$$\sigma = \sigma_0 \exp(-\Delta E_\sigma / k_B T) \quad (2)$$

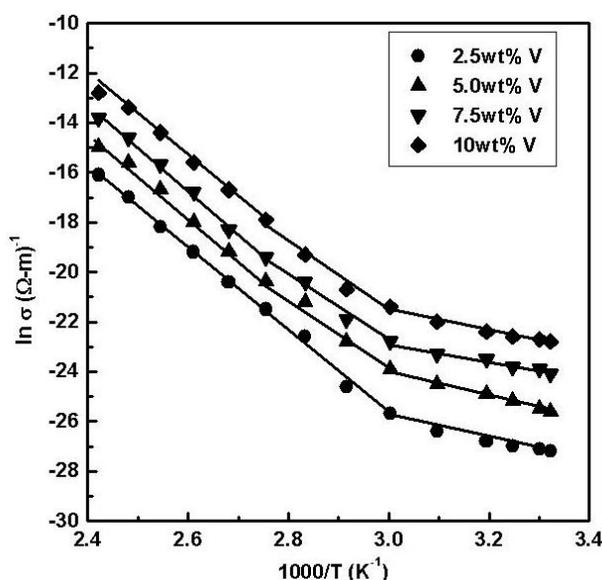


Fig. 1 Variation of $\ln \sigma$ vs. T^{-1} of a 150 nm thick for an undoped ZnTe and four ZnTe:V films.

but can be fitted by a smoothed curve with gradually increasing slope providing a spectrum of activation energies; where ΔE_σ is the activation energy, σ_0 is a constant, k_B is the Boltzmann constant and T is the absolute temperature, respectively. The activation energies are calculated from the local gradients of the $\ln \sigma$ vs. inverse temperature plots which is shown in Fig. 1. The activation energies for four different vanadium doped ZnTe thin films of thickness of 150 nm are tabulated in Table 1. From this table, it may be seen that there is no discrete value of ΔE_σ which covers the whole temperature range but rather a spectrum of activation energies. In this Table, it indicates that the activation energies can be divided into three temperature ranges, such as (i) higher temperature range (363 to 413 K), (ii) intermediate temperature range (333 to 362 K) and (iii) lower temperature range (300 to 332 K), respectively.

It shows that with the increase of temperature, the activation energy is found to increase for all investigated vanadium doped films. So, it is a signature of semiconducting nature. It can be assumed that at higher temperatures, the carriers are activated to the localized states. With the increase of temperature, the activation energy increases indicating that the conduction moves away from the states near the Fermi level. The gradual increase in activation energy may suggest the probability of several impurity levels in the band gap. For

a given temperature, the increase in ΔE_{σ} with decrease in vanadium composition may be connected to the decrease in localized states near the Fermi level.

For comparing the composition dependence of activation energy, it is observed that as the vanadium concentration is increased in the ZnTe dielectric matrix, the value of activation energy is decreased in all investigated samples. Since the activation energy is found to vary with the V-concentration, the results can be interpreted if there is an impurity band conferred to metallic particles in the forbidden gap of ZnTe. According to Devenyi et al. [27], when the metal is highly dispersed, bands of the localized states are expected to appear in the energy band gap of the dielectric matrix. The small activation energies, such as 0.363 eV (at temperature range 300 to 332 K), 0.556 eV (at temperature range 333 to 362 K) and 0.602 eV (at temperature range 363 to 413 K), respectively, in sample (10wt% V, 100 nm) in Table 4.3, indicate that in higher metallic samples the conduction is taking place in the states near the Fermi level. In lower V-concentration, the carriers are activated to take part in the conduction mechanism.

Table 1. Activation energies of undoped ZnTe and doped ZnTe:V thin films.

Thickness	Compositions	Activation energies ΔE_{σ} in (eV)		
		Temperature ranges		
		300-332 K	333-362 K	363-413 K
nm	wt%V	ΔE_{σ} (eV)	ΔE_{σ} (eV)	ΔE_{σ} (eV)
150	2.5	0.475	0.914	0.935
	5.0	0.460	0.825	0.884
	7.5	0.417	0.711	0.757
	10.0	0.363	0.556	0.602

In the compositions $\leq 10\text{wt}\%$ V, the activation energy lies in the range of 0.475 to 0.914 eV in the lower temperature as well as in intermediate temperature range. In this region, the probability of metal-localized state type may increase because; the general trend of the activation energy increases with the increase of ZnTe content. According to Neugebauer and Webb [28], for lower V-concentration, the activation energy will decrease as the island separation is increased, and hence the probability of activated tunneling is diminished. In author's sample with lower vanadium concentration ($\leq 10\text{wt}\%$ V), direct tunneling would also be limited by the large particle separation. When the island gaps are large, the probability of thermionic emission may only be considered if the value of activation energy becomes smaller [29]. However, it is evident in the present samples that the activation energy becomes large as ZnTe content increases. Therefore, metal-metal tunneling may be eliminated because the activation energy is a function of temperature. Activation energy of author's sample does agree well with the reported value [20].

3.2 Optical Studies

To study the optical properties of ZnTe:V thin films, the films of various compositions are deposited onto glass substrates. Transmittance and reflectance spectra of ZnTe:V films are recorded by spectrophotometer as a function of the wavelength for each sample of different compositions, respectively. Figures 2(a) and (b) show the transmittance and reflectance spectra as a function of wavelength of 150 nm thick ZnTe:V films for various compositions, respectively. Figure 2(a) shows the feature of transmittance spectra that is decreased with increasing vanadium compositions up to infrared region.

In Fig. 2 (b), the reflectance spectra indicate the feature that in the visible region, it has a reflectance value of 0.33 and its value decreases with the increase of vanadium doping up to $\lambda = 650$ nm. It then shows a signature of interference in the reflectance spectra for all vanadium compositions in the near infrared wavelength range.

The absorption coefficient (α) is calculated from recorded transmittance and reflectance data of ZnTe:V samples for different compositions using the following relation as Pankove [30].

$$\alpha = \frac{1}{t} \ln \left[\frac{1-R^2}{T} \right] \quad (3)$$

where T is the transmittance, R is the reflectance and t is the thickness of the film. In the high absorption region, energy band gap of ZnTe:V thin films can be obtained by the relation as Pankove [30],

$$\alpha h\nu = B(h\nu - E_g)^P \quad (4)$$

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, direct allowed, indirect forbidden and direct forbidden transitions, respectively. The usual method for determining the value of the band gap (E_g) involves, plotting a graph of $(\alpha h\nu)^{1/P}$ versus photon energy (h ν) in accordance to Eq. 4.

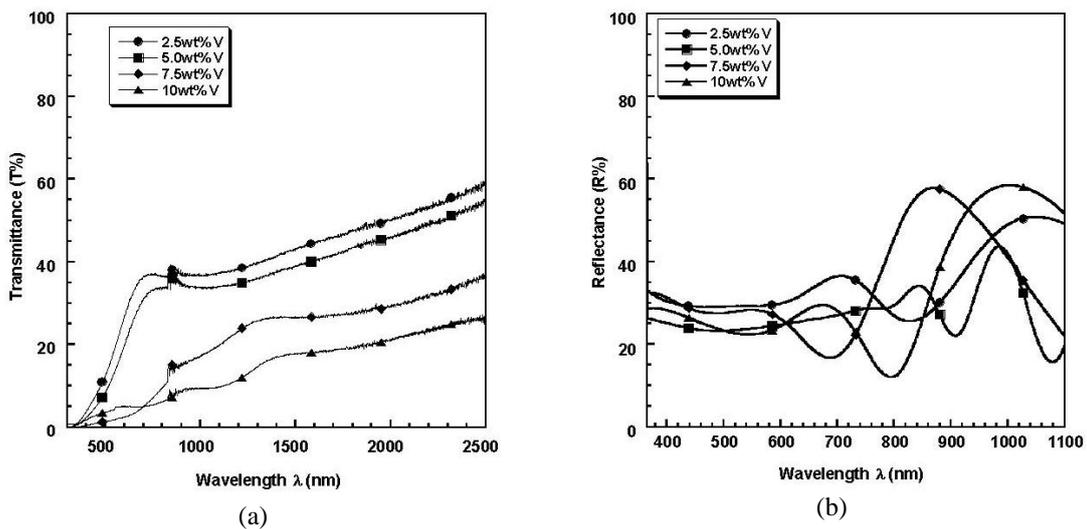


Fig. 2 (a) Transmittance and (b) reflectance spectra of 150 nm thick ZnTe:V samples for various compositions.

If an appropriate value of P is used to obtain 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. It is seen from all the curves that the best fit plot is plot $(\alpha h\nu)^2$ - $h\nu$ which covers the widest range of data. The best fit plots of the ZnTe:V thin films for different compositions are shown in Fig. 3.

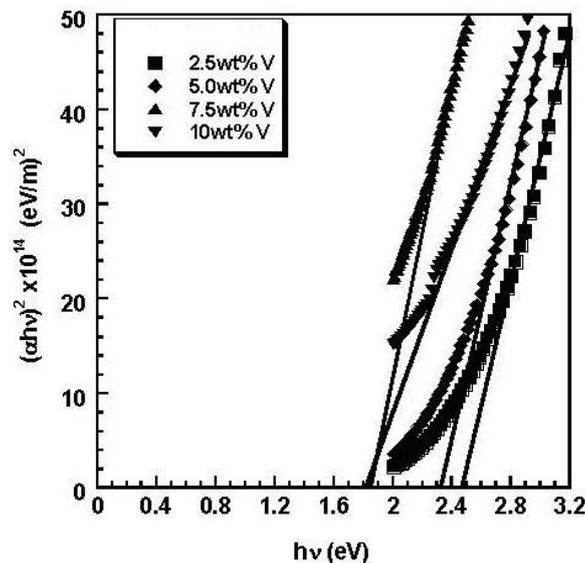


Fig. 3 Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for 150 nm thick ZnTe:V films for different compositions.

The band gap (E_g) is obtained by extrapolating the curves to $(\alpha h\nu)^2 = 0$ for direct allowed transition. The estimated values of E_g for various compositions are ranged of 1.82 to 2.48 eV, respectively. The corresponding calculated values of constant B (using Eq. 4) lie in the range of 0.87×10^8 to $0.81 \times 10^8 \text{ m}^{-1} \cdot \text{eV}^{1/2}$, respectively. The values of E_g and B for various compositions are tabulated in Table 2. The author’s result of E_g for ZnTe:V samples do agree well with that of ZnTe value reported by and Rusu et al. [18].

To calculate the refractive index, n and extinction coefficient, $k_o(=\alpha\lambda/4\pi)$, the method suggested by Manifacier et al. [31,32] 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 [33].

$$T = \frac{16 n_a n_g n^2 \exp(-\alpha t)}{R_1^2 + R_2^2 \exp(-2\alpha t) + 2 R_1 R_2 \exp(-\alpha t) \cos\left(\frac{4\pi n t}{\lambda}\right)} \quad (5)$$

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 $\epsilon_1 = n^2 - k_o^2$ for different compositions of 150 nm thick films. The refractive index of ZnTe:V is calculated using Eq. 5. The values of refractive indices lie within the range of 2.94 and 3.20, respectively. The dielectric constant that gives the value ranged between 8.64 and 10.24, respectively. The values of refractive index and dielectric constant for different compositions are listed in Table 2. Author's results of n and ϵ_1 do agree well with the reported results [10].

Table 2 Optical parameters for 150 nm thick ZnTe:V films at different compositions.

Compositions wt% V	E_g (eV)	$B \times 10^8$ ($m^{-1} \cdot eV^{-1/2}$)	n	k_o	ϵ_1
2.5	2.48	0.81	2.94	0.53	8.64
5.0	2.33	0.81	3.01	0.64	9.06
7.5	1.85	0.65	3.08	1.11	9.49
10.0	1.82	0.87	3.20	0.86	10.24

Table 2 shows the evaluated values of different optical parameters for 150 nm thick ZnTe:V films of various compositions. From this Table it is clear that the values of n and ϵ_1 are found to increase monotonically whereas the values of E_g are seen to decrease with increasing vanadium content. It is also observed that the values of k_o and B do follow a disproportionate variation with the variation of vanadium content in ZnTe:V films.

3.3 Electronic band structure

Electronic band structure determination is very important to characterize the material. In that sense it is determined by comparing the values of obtained dc activation energy ΔE and band gap E_g of ZnTe:V thin films for different vanadium compositions. The activation energy is taken from Table 1 in the reasonable temperature range of different concentrations and corresponding optical band gap E_g is taken from Table 2. By comparing it is seen that the value of ΔE is much less than the half of optical band gap E_g . This lower value indicates the existence of impurity levels within the mobility gap (i.e. gap between conduction and valence band edges) and determines both the activation energy and carrier mobility. It is well known that disordering in amorphous materials gives rise to localized state in the band gap. The optical absorption measurement gives the evidence for the existence of localized tail state which increases with V-concentration in ZnTe films. Hence, it may be concluded that in ZnTe:V system, there exists not only the inherent disordering that is common to an amorphous materials but also be disordered arising from the presence of vanadium in the ZnTe matrix. If the density of localized levels is high enough, hopping between these levels to be expected.

A rough sketch of the electronic band structure is done of 150 nm thick ZnTe:V thin films of 2.5wt% V composition in the insulating regime by taking into account the results of dc activation energy 0.475 eV (from Table 1) and optical band gap 2.48 eV (from Table 2). This rough sketch is shown in Fig. 4.

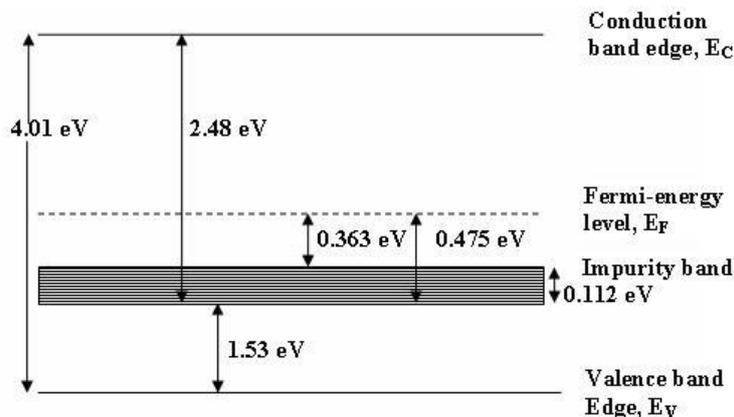


Fig. 4 Calculated electronic band structure for band gap 2.48 eV of a thick 150 nm of 2.5wt% V doped ZnTe:V thin film.

In doing so, it is assumed that the Fermi level is roughly midway between the valence and conduction bands. The position of Fermi level within the mobility gap is obtained at 2.005 eV from conduction or valence band edge. It is seen from Table 1 that irrespective of vanadium concentration, the activation energy at room

temperature varies from 0.363 to 0.475 eV and the difference between them 0.112 eV which value is supported by Hill's generalized model (not shown). The tail states of valence and conduction bands are most probably created by the presence of structural defects in ZnTe matrix. The introduction of vanadium into ZnTe matrix gives rise to disorder or defects, which causes the extension of tail states in the energy band gap and produces a narrow impurity band at about 0.363 eV below the Fermi level, E_F . Thus combining knowledge of the activation energy with the estimated optical band gap, a value of 4.01 eV is obtained for the mobility band gap. It should be noted that an impurity band lies at 1.53 eV above the valence band for optical band gap of 2.48 eV of 150 nm thick ZnTe:V film of composition 2.5wt% V. Similarly, the calculated positions of impurity band lie at 1.38, 0.90 and 0.87 eV above the valence band for band gaps of 2.33, 1.85 and 1.82 eV of compositions 5.0, 7.5 and 10wt% V of 150 nm thick ZnTe:V films, respectively. The average value of these energy positions of impurity bands of author's sample is 1.17 eV which is agreed well with the reported value of 1.17 eV for ZnTe:V [11] films.

IV. Conclusions

ZnTe:V of various vanadium compositions were prepared onto glass substrate by e-beam evaporation technique in vacuum at 8×10^{-4} Pa. The deposition rate of the films was maintained at 2.052 nms^{-1} . X-ray diffraction study indicates that the ZnTe:V films are mixed crystalline in structure. Electrical and optical properties of ZnTe:V thin films were studied in detail for various vanadium compositions. Temperature dependence of electrical conductivity exhibited a semiconducting behavior. Dopant vanadium concentration increases the conductivity of the samples. It is seen that electrical conduction of ZnTe:V thin films obey the thermally activated conduction mechanism. Different optical parameters of ZnTe:V thin films were investigated. Electronic band structure of ZnTe:V thin films are determined using these electrical and optical properties. Evaluation of these parameters may help in view of their technological applications in optoelectronic devices

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