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EFFECTS OF VARIOUS PARAMETERS ON THE DC ELECTRICAL PROPERTIES OF ZnTe:V THIN FILMS

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The vanadium doped zinc telluride (ZnTe:V) as well as ZnTe thin films and their sandwich structures were prepared onto glass substrate by e-beam evaporation technique in vacuum at a pressure of $\sim 8\times10^{-4}$ Pa. The effects of various parameters on the dc electrical properties of the sandwich Al/ZnTe:V/Al structure have been studied in detail. It is found that the effects of ambient pressure, source to substrate height, beam current, composition, thickness, temperature, aging and annealing play important role in the obtaining sandwich structures. The current voltage characteristics of ZnTe:V films (containing 0 to 10wt% V) were studied under the electric field ($>10^5$ Vm^{-1}) as a function of film thickness ranges of 100 to 250 nm. The investigated temperature was 300 to 413 K. Thermopower measurement was also done in the above temperature range. The results of conductivity and thermoelectric power of ZnTe:V thin films obey the thermally activated conduction mechanism. Thermopower result of ZnTe thin film shows a p-type carrier whereas vanadium doped ZnTe films also suggest that the simultaneous bipolar conduction of both carriers take place.

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Activation energy, Electric field, Thermopower

1. Introduction

In recent years, the compound semiconductors of II-VI family, in particular Zinc Telluride (ZnTe) has been focus of great interest due to its low cost and high absorption co-efficient for application to photovoltaic and photoelectrochemical cells [1-4]. ZnTe has a direct band gap of 2.2 to 2.3 eV at room temperature and usually a p-type semiconductor. Literature report [5] indicates that ZnTe exhibits improved photorefractive response when it is doped with vanadium. Vanadium is believed to be a deep donor in ZnTe and it has attractive use in a variety of applications, including optical power limiting, optical computing and optical communication [6]. Moreover, ZnTe:V offers superior photorefractive performances for the application of optical data processing and power combining in operation of 800 to 900 nm band region compared with the large band gap semiconductor such as GaAs as CdTe where their energy band gap limit their use below ~900 nm.

Although there have been a number of investigations on the electrical [7,8], optical [9,10] and electrooptical properties of ZnTe [7,9,11] and ZnTe:V [5,6] materials by a number of researchers but no systematic study has been done on the electrical and optical properties, in particular on vanadium doped ZnTe films, at varying deposition conditions. Hence, there is a need to study how varying deposition conditions affect the dc electrical properties of vanadium doped

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ZnTe thin film to assess its usefulness in a variety of optoelectronic devices. In this paper, we discussed the effects of various parameters on the dc electrical properties of ZnTe:V thin films.

2. Experimental

2.1. Film preparation

The ZnTe:V thin films, containing a mixture of ZnTe powder (99.999% pure) and vanadium powder (99.999% pure), obtained from Aldrich Chemical Company, U.S.A., were deposited by electron bombardment heating technique in vacuum (Coating unit: Edwards, model: E306) at a pressure of 8×10^{-4} Pa. Each material of ZnTe:V was weighted by an electronic balance (Mettler TOLEDO, AB 204) which has a resolution of ±0.0001 g, according to percentage of composition to be used. The percentage of composition of the starting materials in the evaporant mixture was determined as the followings [12]

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

where W_v and W_{ZnTe} are the weights of vanadium and ZnTe, respectively. Then the materials were grinded together using a pestle and mortar and mixed thoroughly. The lower and upper Al (Aluminium) electrodes of sandwich devices were evaporated during the same pump down cycle. Three masks (one for ZnTe:V films and others two for electrodes) were used for the deposition of sandwich devices. A mechanical shutter was isolated the substrate from the evaporants and it was operated from outside.

The deposition chamber was thoroughly cleaned with emery paper and cotton-wool by wetting acetone and then it was dried with a dryer. A small quantity of source materials was loaded into clean cermet-hearth based on the source turret. Required masks were placed on the mask holder according to the demand of shape of the film. Cleaned substrates were placed on the substrate-holder about 9 cm above the source material and thereafter the chamber bell jar was placed on the base plate. 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 of the electron beam supply (EBS) unit. The sandwich ZnTe:V thin films (containing 0 to 10 wt% V) of thickness range of 100 to 250 nm were deposited onto substrate. The Al/ZnTe:V/Al sandwich devices [13] were deposited onto glass substrates at room temperature for measuring I-V characteristics at various conditions and its schematic diagram is shown in Fig. 1. The deposition rate was obtained ~2.05 nms^{-1}.

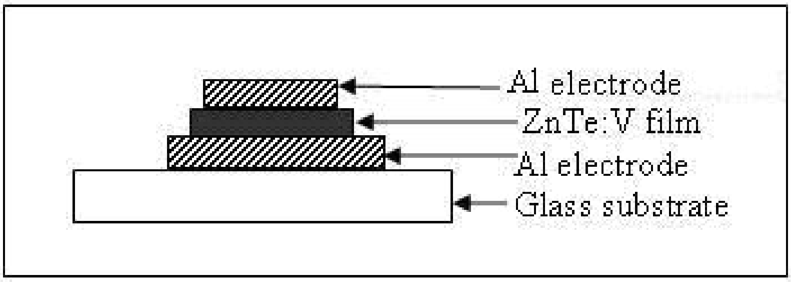

Fig. 1. Schematic diagram of sandwich structure of Al/ZnTe:V/Al.

2.2. Measurement technique

I-V characteristics of sandwich Al/ZnTe:V/Al structures were measured as a function of temperature in the range of 300 to 413 K. The glass substrate was heated by a specially designed heater and the temperature was measured by a chromel-alumel thermocouple placed on the middle of the substrate. 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) was used to monitor the current through the sample and a digital multimeter (Model: DM-206) was used to measure the potential difference across each sample. Digital multimeter (Model: DL-711) was also used to measure the current. The thickness was measured by the Tolansky [14] interferometry method with an accuracy of ± 5 nm.

3. Results and discussion

When insulating or semiconducting thin film is sandwiched by two metal electrodes of same materials and if there is no sudden increase of conductivity is seen with applied voltage at any condition then that device is also called the unformed (Al/ZnTe:V/Al) device. Different effects of various parameters play important role on conductivity of unformed device. These effects are discussed below step by step.

3.1 Effect of electrode materials

To compare the effects of electrode materials on I-V characteristics, three types sandwich devices of same electrode materials, such as Al/ZnTe:V/Al, Ag/ZnTe:V/Ag and Cu/ZnTe:V/Cu were prepared onto glass substrate at the same ambient condition. I-V graph of each device for a 150 nm thick ZnTe:V film of composition 2.5wt% V is shown in Fig. 2. It is seen from the graphs that the electrical conduction mechanism appears to be independent of electrode materials. On the other hand, it depends on the relative work functions of used electrode materials and the film material. It is noted that the work function is different in values for different film materials. It is also observed that the current conduction in Al/ZnTe:V/Al device is higher than that of Ag/ZnTe:V/Ag or Cu/ZnTe:V/Cu device. It is also seen that current through the Ag/ZnTe:V/Ag device is greater than that of Cu/ZnTe:V/Cu up to the electric field of 1.33×10^{8} Vm^{-1} and beyond this field the current in Cu/ZnTe:V/Cu device is higher than that of Ag/ZnTe:V/Ag device.

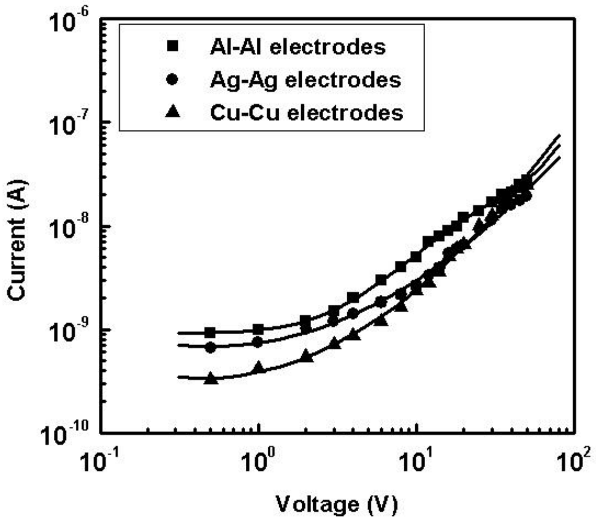

Fig. 2. I-V curves for Al-Al, Ag-Ag and Cu-Cu electrodes for a thick 150 nm ZnTe:V films deposited at composition 2.5wt% V.

3.2. Effect of compositions

The ZnTe:V sandwich film contains a mixture of vanadium powder in zinc telluride matrix is very important. To study the effect of vanadium composition, five samples each of 150 nm thick Al/ZnTe:V/Al structure were deposited with different compositions of 0.0, 2.5, 5.0, 7.5 and 10wt% V, respectively at a pressure of ~8×10^{-4} Pa and their I-V characteristics are shown in Fig. 3. The curves show that as the vanadium concentration increases, the higher current flowing through the devices. These effects may be due to the cause of metallic filaments are formed in the samples of higher vanadium content. Inter metallic island distance is decreased with the increase of vanadium concentration in ZnTe matrix.

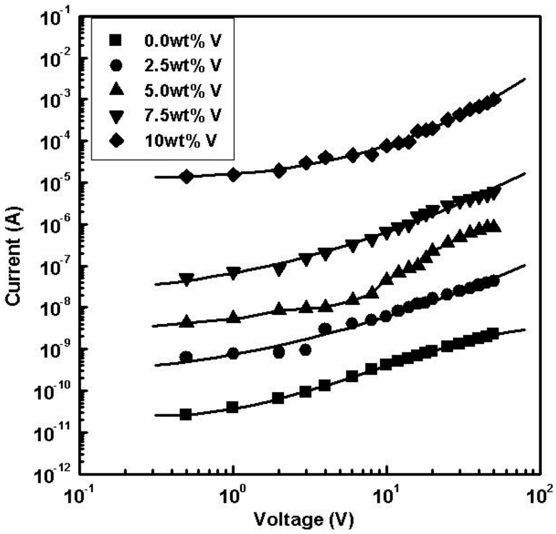

Fig. 3. I-V curves for a 150 nm thick Al/ZnTe:V/Al devices deposited at variable compositions.

3.3. Effect of thickness

Effect of thickness on I-V characteristics of Al/ZnTe:V/Al devices of thickness of 100, 150, 200 and 250 nm, respectively deposited at a fixed composition of 2.5wt% V are shown in Fig. 4. It is seen from the graphs that the conduction of the system increases with the decreasing of thickness. This may be due to the increase of inter metallic island distance with the increase of film thickness. As a result impedance of devices increases with the increase of its thickness.

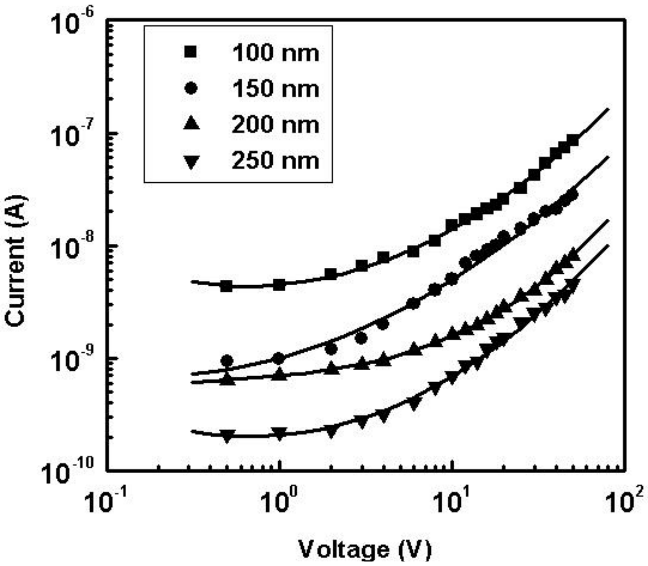

Fig. 4. I-V curves of Al/ZnTe:V/Al structures deposited at 2.5wt% V at variable thicknesses.

3.4. Effect of ambient pressure

The effect of ambient pressure on I-V characteristics of a sandwich Al/ZnTe:V/Al device of thickness 150 nm at a composition of 2.5wt% V is shown in Fig. 5. It is observed from the graphs that with the decrease of ambient pressure, the device conductivity is found to increase in all investigated structures at room temperature. It may be the caused of the reduction of oxygen particles in the films with the higher of ambient pressure. The main feature of the conduction of the system is that it exhibits ohmic behaviour in low field (< 6.67×10^6 Vm^{-1}) region but non-ohmic behaviour in the high field region 6.67×10^6 to 3.33×10^8 Vm^{-1}.

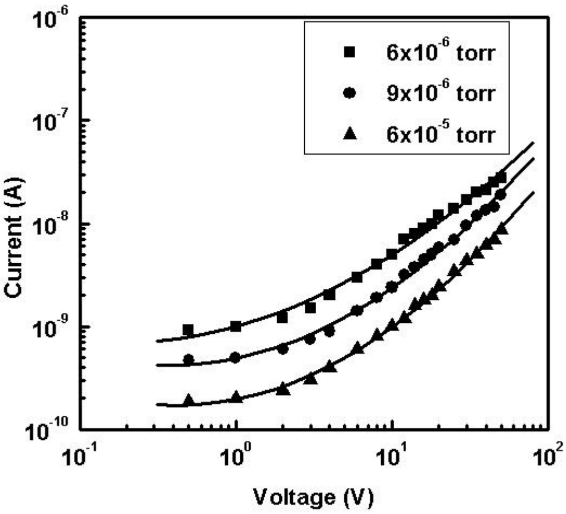

Fig. 5. I-V curves of a 150 nm Al/ZnTe:V/Al film deposited at 2.5wt% V.

3.5. Effect of source to substrate distance

Three sets of each 150 nm thick Al/ZnTe:V/Al structure with composition of 2.5wt% V were deposited at a various source to substrate heights of 0.08, 0.09 and 0.10 m, respectively which is shown in Fig. 6. The dc I-V characteristics of their study indicates that the structure is grown at source to substrate height of 0.09 m offers the highest conduction relative to others.

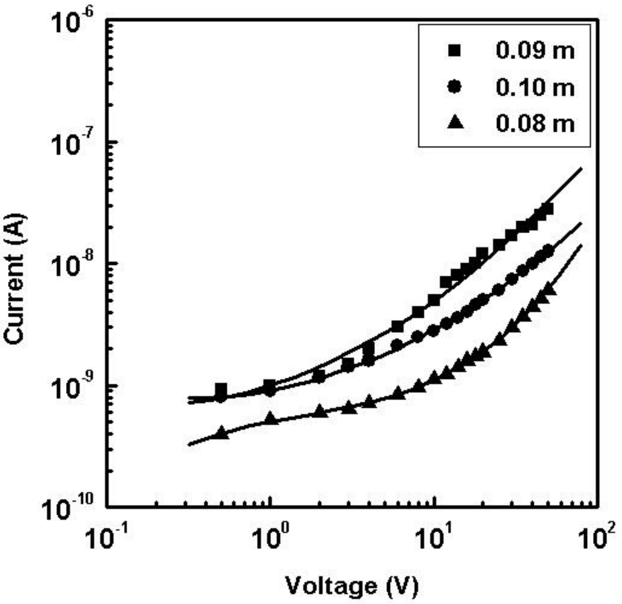

Fig. 6. I-V curves of different substrate distances of a 150 nm Al/ZnTe:V/Al structure deposited at 2.5wt% V.

3.6. Effect of beam current

The role of e-beam current in devices has been studied in details. Three samples of a 150 nm thick Al/ZnTe:V/Al structure of composition 2.5wt% V were deposited at a beam current of 40, 45 and 50 mA, respectively with a pressure of 8×10^{-4} Pa and their results are shown in Fig. 7. It indicates from the graphs that the conduction increases with the increasing of beam current. The cause of the increase is due to the increasing of particle compactness and the increase of metal islands in the deposited structure.

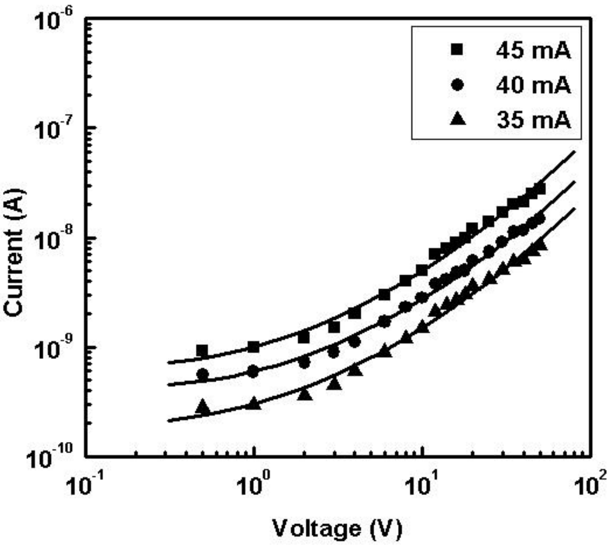

Fig. 7. I-V curves of different beam current for a 150 nm sandwich devices grown at 2.5wt% V.

3.7. Effect of temperature

Al/ZnTe:V/Al sandwich device of a 150 nm thickness was deposited onto glass substrate at a particular film composition of 2.5wt% V. The I-V characteristics of Al/ZnTe:V/Al sandwich device were studied for different temperature of 303, 333, 363 and 393 K, respectively and their results are shown in Fig. 8. The curves of this figure show that the device current is increased with the increase of film temperature for the investigated voltage range. The nature of curves indicates the semiconducting property.

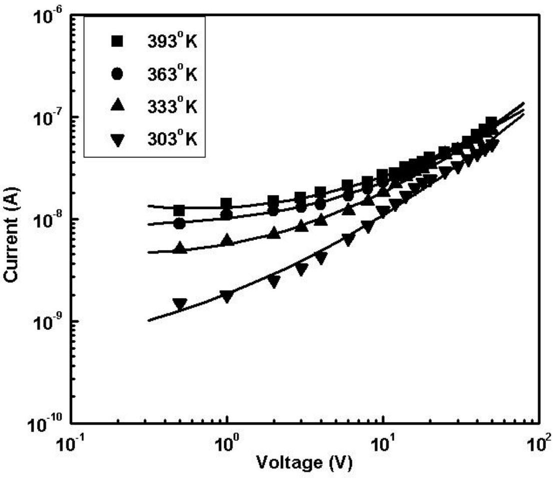

Fig. 8. I-V curves of Al/ZnTe:V/Al structures deposited at 2.5wt% V at various temperatures.

3.8. Effect of annealing

To study the effect of annealing on the I-V characteristics of the film devices, the sample Al/ZnTe:V/Al was annealed at 473 K for 3 hours in air. After annealing, the effects were investigated at room temperature. The graphs of the as-deposited and annealed devices at a composition 2.5wt%V of thickness 150 nm are shown in Fig. 9. It is seen from the graphs that for the annealed device, the film resistance is decreased and its corresponding current is increased by an order of magnitude at a potential difference 0.5 to 2 V compared to the values of as-deposited one. The reasons behind the increase is that due to annealing some resistive elements *i.e.* atmospheric or air particles within the films are diminished which causes a low resistive structure of the films.

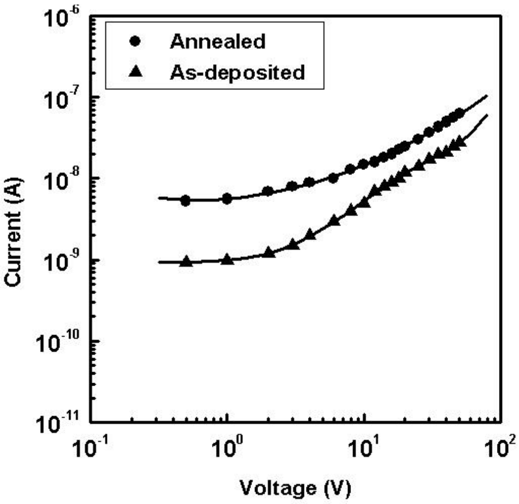

Fig. 9. I-V curves for a as-deposited and annealed Al/ZnTe:V/Al films deposited at 2.5wt% V.

3.9. Electrical properties

Electrical conductivity σ was measured as a function of temperature in the 300 to 413 K ranges. The glass substrate was heated by a specially designed heater and the temperature was measured by a chromel-alumel thermocouple placed on the middle of the substrate. The conductivity was obtained by applying a dc 15 V bias across the film with silver contact and recording the current and voltage simultaneously by using a standard sandwich method. Fig. 10, reports ln σ vs. 1/T curves for five samples each 100 nm in thick, ZnTe:V films of compositions 0.0, 2.5, 5.0, 7.5 and 10wt% V, respectively. It is interesting to note that conductivity appears to vary continuously with inverse temperature suggesting a thermally activated conduction mechanism. The conductivity of these samples cannot be represented by one single exponential form expressed as Criado et al. [16] as followings

$$\sigma = \sigma_0 \exp(-\Delta E_\sigma / k_B T) \tag{2}$$

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_o is a constant and k_B = Boltzmann constant, respectively. The activation energies are calculated from the slopes of the local gradients of the ln σ vs. inverse temperature plots. From these plots, the activation energies for four different vanadium doped and an undoped ZnTe thin films of thickness of 100, 150 and 200 nm, respectively are shown in Table 1. From Table 1 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 [17, 18].

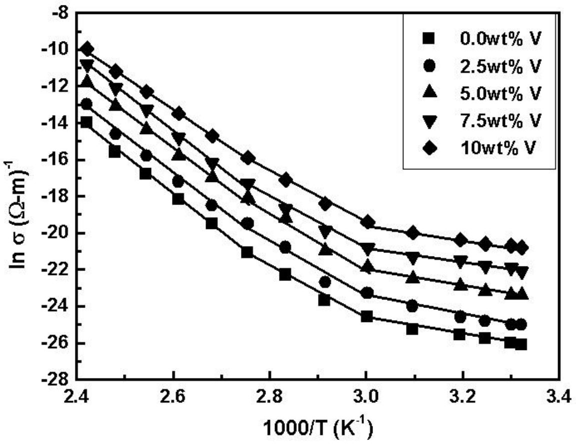

Fig. 10. Variation of lnσ vs. T^{-1} for five compositions of ZnTe:V devices for a thick 100 nm.

It shows that with increase of film thickness, the corresponding activation energy is found to increase for all investigated ZnTe thin films. It is clear from this Table 1 that with the increase of temperature, the activation energy is found to increase for all investigated V-doped and undoped films. So, 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. [19], 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 0.34 eV (at temperature range 300-332 K), 0.52 eV (at temperature range 333-362 K) and 0.61 eV (at temperature range 363-413 K), respectively in sample [10wt% V, 100 nm] in Table 1, 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.

In the compositions ≤ 10wt% V, the activation energy lies in the range of 0.47 to 0.91 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 [20], 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 (≤ 10wt% 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 [21]. 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. Error of activation energy was calculated in percentage for all samples using simple statistical standard deviation method and it is shown in Table 1.

Table 1. Activation energies of ZnTe:V sandwich devices.

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)	Error analysis (%)	ΔE_σ (eV)	Error analysis (%)	ΔE_σ (eV)	Error analysis (%)
100	0.0	0.48	0.34	0.90	0.59	0.96	0.65
	2.5	0.47	0.43	0.89	1.40	0.93	1.29
	5.0	0.44	0.29	0.79	1.00	0.87	1.02
	7.5	0.40	0.30	0.65	0.83	0.73	0.91
	10.0	0.34	0.40	0.52	0.54	0.61	0.53
150	0.0	0.50	0.35	0.95	0.35	0.98	0.24
	2.5	0.48	0.40	0.91	0.87	0.94	0.31
	5.0	0.46	0.16	0.83	0.69	0.88	0.78
	7.5	0.42	0.28	0.71	0.65	0.76	0.70
	10.0	0.36	0.36	0.56	1.13	0.60	0.78
200	0.0	0.51	0.11	0.97	0.13	1.04	0.33
	2.5	0.50	0.18	0.87	0.86	1.01	0.50
	5.0	0.47	0.14	0.85	0.35	0.99	0.39
	7.5	0.44	0.26	0.75	0.71	0.86	0.28
	10.0	0.42	0.33	0.62	0.89	0.75	0.89

3.10. Thermoelectric effect

The thermoelectric power measurements of ZnTe:V films were carried out by integral method [22]. Fig. 11 shows the thermopower vs. temperature curves for five ZnTe:V thin films containing 0 to 10wt% V in the temperature range of 303 to 413 K, respectively. Seebeck voltage was measured with respect to a copper contact film by connecting the positive terminal of the electrometer to the cold open end and negative to hot end. From this study, it is seen that the value of thermopower and the form of its dependence on temperature is varied markedly.

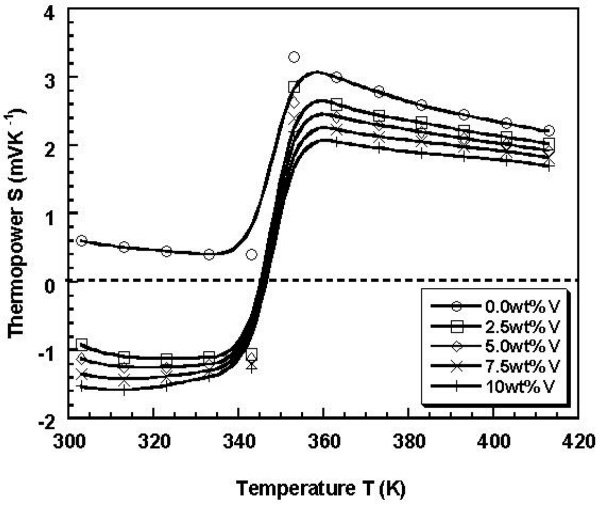

Fig. 11. Variation of thermopower with temperature for a 150 nm thick ZnTe:V thin films of different compositions.

The undoped ZnTe films show a positive thermopower indicating a p-type semiconductor [23]. In the composition of 2.5 to 10wt% V, the positive component of the thermopower dominates at higher temperature, the peak thermopower increases with decreasing metal V content. All investigated samples show mixed-carrier behaviour except in undoped ZnTe films. The thermopower decreases slowly up to 343 K, then starts to increase abruptly, a sign reversal occurs at 348 K and then increases positive up to 353 K, beyond of this temperature the thermopower starts to decrease [17]. These curves show that the thermopower is thermally activated within the temperature range of 343 to 353 K for all the samples containing 2.5 to 10wt% V content. The compositional dependence of conduction may be explained by supposing that the Fermi-level is pinned midway between the conduction and valance bands as discussed by Mott [24]. The low thermopower values indicate that the position of the impurity band due to V in the ZnTe matrix is considered to coincide with the Fermi-level.

4. Conclusions

Vanadium doped ZnTe thin films and its sandwich structures of composition 0 to 10wt% V of thickness 100 to 250 nm, were prepared onto glass substrate by e-beam evaporation technique in vacuum at 8×10^{-4} Pa. The effects of various parameters such as ambient pressure, source to substrate height, beam current, doping composition, thickness, temperature and annealing on dc electrical properties of ZnTe:V thin films have been studied in detail and their effects play an important role in the conduction mechanism of the sandwich devices. The deposition rate of the film was maintained at 2.05 nms^{-1}. The thickness, composition and temperature dependence of the activation energy as well as thermoelectric power measurements were done in the temperature range of 300 to 413 K. The value of activation energy 0.48 eV of undoped ZnTe is good agreement with published value of the Bellakhder et al. of activation energy of ZnTe. The results of dc conductivity and thermoelectric power obey an activated conduction mechanism. Thermopower results of the undoped ZnTe films show a positive thermopower indicating a p-type semiconductor whereas vanadium doped ZnTe also suggests that the simultaneous bipolar conduction of both carriers take place.

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