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Studies on the Seebeck effect in semiconducting ZnO thin films

M. G. AMBIA, M. N. ISLAM, M. OBAIDUL HAKIM*
*Department of Applied Physics and Electronics, and *Department of Physics, University of Rajshahi, Rajshahi, Bangladesh*

For ZnO thin films prepared by a pyrolytic technique, the thermoelectric power has been measured from room temperature up to 200 °C with reference to pure lead. The thickness and temperature dependence of its related parameters have been studied. The Fermi levels were determined using a nondegenerate semiconducting model. The carrier scattering index, activation energy and temperature coefficient of activation energy, have all been obtained at different ranges of thickness and temperature. All the samples were polycrystalline in structure and optically transparent.

1. Introduction

Zinc oxide thin films have long been known to be transparent conducting materials [1]. They are very useful as solar cell materials, and for various other electrical and optoelectronic devices where energy efficiency is of concern. Like most of the pure oxide crystals, undoped ZnO is normally an electrical insulator. But its electrical conductivity as practically observed is due to the presence of many crystal defects such as a stoichiometric excess of zinc and vacancies introduced in the sample during the process of sample preparation. Usually ZnO thin films are considered to be n-type wide band gap semiconductors [1].

Because thermoelectric power (TEP) is the most sensitive quantity to any change or distortion of the Fermi surface in the material, measurement of TEP would be a useful technique for investigating the electronic conduction process in such a sample. In this paper we report some results of the measurement of TEP in ZnO thin films. There are various methods of preparing ZnO thin film. In the present study we used the so-called pyrosol process [2] to deposit ZnO films of desired thickness. These films were non-stoichiometric and were highly transparent on glass substrates. The films were between 95 and 210 nm thick. A survey of the scientific literature shows that studies on TEP are not common for spray-deposited ZnO thin film. Some measurements on ZnO bulk crystals have been reported by Hutson [3] and Hogarth [4], but other reports include measurement mostly on electrical conductivity, Hall effect and effects of heat treatment [5].

2. Experimental procedure

With 0.4 M aqueous solution of zinc acetate, $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, in a pyrex flask, an aerosol is prepared using a pneumatic spray gun and compressed air. The aerosol is then carried to the pyrolysis section by the same in-flowing air. In this section of the apparatus a heater is situated, over which the substrate is placed on a thick stainless steel platform. When the reacting aerosol reaches the hot substrate surface, hydrolysis of zinc acetate takes place and ZnO is formed as a thin film on the glass substrate. The probable reactions include

$$Zn(C_2H_3O_2)_2 \cdot 2H_2O + H_2O \xrightarrow{\text{heat}} ZnO + 2CH_3COOH + 2H_2O \quad (1)$$

The substrate temperature was ~ 360 °C and was kept constant for the present set of samples. A few drops of acetic acid make the acetate-containing working liquid clear and suitable for easy spraying. Details of the film deposition process can be obtained elsewhere [6].

All the samples were then annealed in vacuum before using for any measurement. This was necessary because the as-deposited samples were of very high resistivity. The annealing variables were vacuum pressure 2×10^{-5} torr (1 torr = 133.322 Pa), maximum temperature 250 °C for a period of 1 h, and average cooling rate 2.5 °C min^{-1}. For TEP measurements pure lead was used as reference metal, therefore a pure lead thick film was deposited on the sample substrate, as shown in Fig. 1, by thermal evaporation of metallic lead. During pyrolysis two films were prepared in a single run, one for thickness, conductivity and Hall effect studies, and the other for TEP measurement. An appropriate masking arrangement gives the proper shape of the experimental sample.

For electron microscopic studies, films were deposited on NaCl substrates. After immersion in water the films were then carefully taken on a copper grid for further investigation by TEM. The film thickness was determined by the Tolansky interferometric method and the van der Pauw method was employed to study the Hall effect and electrical conductivity. Measurement of TEP was carried out by the integral method [7], in which junction A was heated by a flat nichrome

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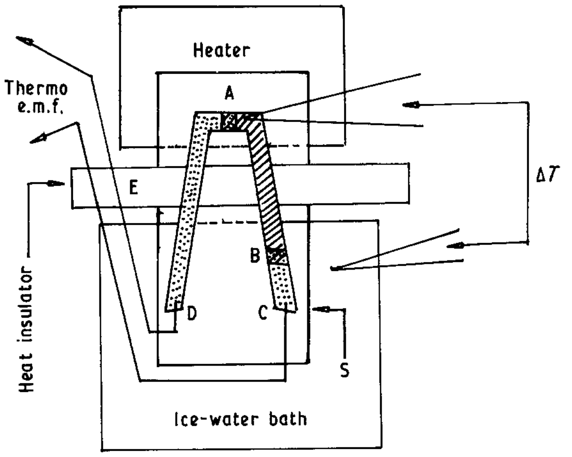

Figure 1 Schematic diagram of thermopower measuring apparatus: AB, ZnO film; DA and BC, lead films; S, substrate; E, heat insulating barrier; ΔT is the temperature difference between hot and cold ends.

strip heater with regulated power supply to keep it at different temperatures. A spring pressure clipping arrangement provided a close contact between the heater and the sample. The other junction, B, was immersed in an ice–water bath of constant (0 °C) temperature. The temperature of the hot junction was measured using a chromel–alumel thermocouple attached to the sample. The generated thermo e.m.f. was recorded using a digital voltmeter. The hot and cold junctions were kept thermally isolated by inserting an insulated barrier between the junctions. The immersed portion of the film was kept electrically insulated to remove any leakage of e.m.f. between D and C due to contact with the ice–water. The whole apparatus was kept in a suitable enclosure to minimize any air-current disturbances. The temperature of the hot junction was raised slowly from room temperature, and at regular intervals of 5 °C the thermo e.m.f. was noted up to the highest temperature of 200 °C.

3. Results and discussion

It has been found from electron microscopic investigation that the samples are polycrystalline in structure with small grains uniformly oriented over the substrate surface. Fig. 2 shows the values of thermo e.m.f. at different temperatures for four samples of different thicknesses. It is observed that the thermo e.m.f. is positive with respect to lead. Fig. 3 shows the variation of the corresponding thermoelectric power, Q, with inverse temperature. It is observed from this figure that the thermopower decreases continuously with increasing temperature and saturates in the higher temperature region. The rate of change of Q with temperature is greater for films of higher thickness than for lower thickness. The saturation of Q with temperature also occurs at relatively higher temperature in the thicker films than in thinner films. At a fixed temperature the variation of thermopower with film thickness is as shown in Fig. 4.

Because Hall measurements on these samples show n-type conductivity, the thermopower should be negative. However, our present measurements on these

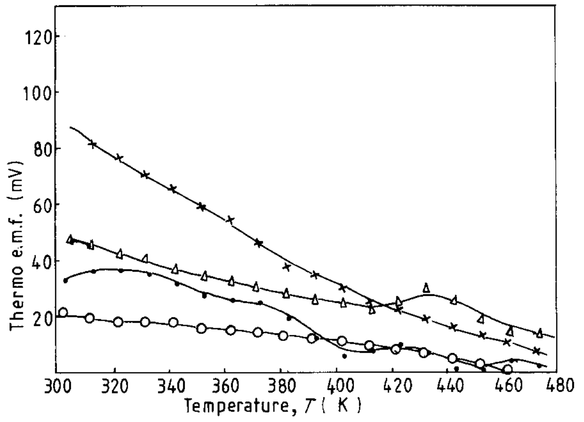

Figure 2 Variation of thermo e.m.f. with temperature of ZnO films of different thickness: (×) 205.8 nm, (△) 149.1 nm, (●) 131.3 nm, (○) 95.3 nm.

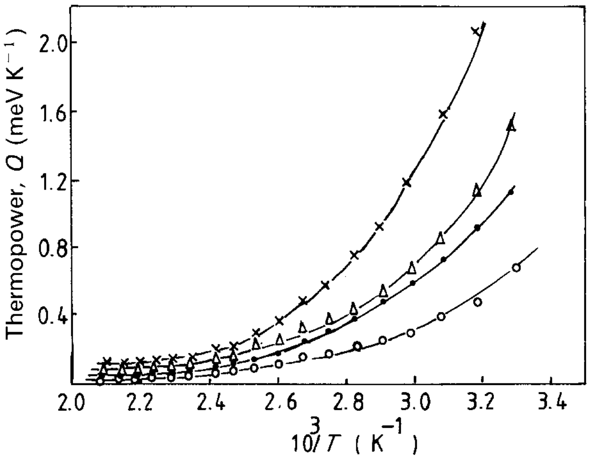

Figure 3 The plot of thermopower, Q, against inverse of temperature of ZnO films of various thickness. For key, see Fig. 2.

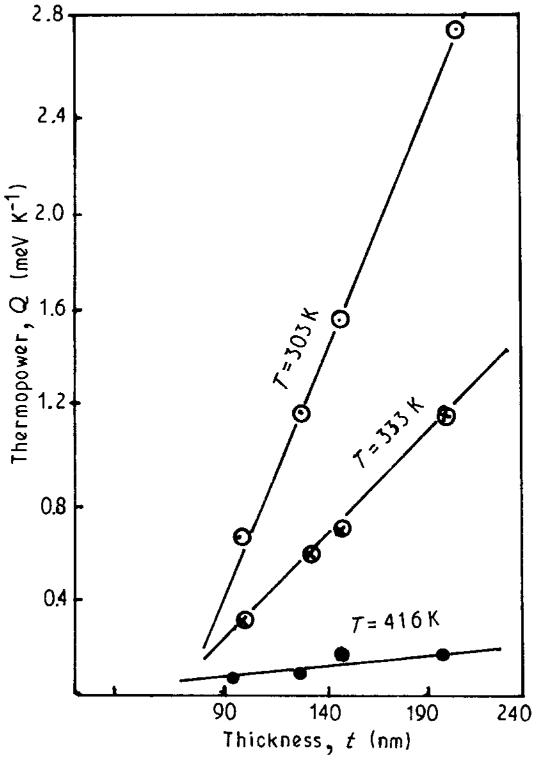

Figure 4 The variation of thermopower of ZnO film as a function of thickness at three different temperatures.

annealed samples show a positive thermopower indicating a p-type behaviour. There are many situations when an n-type material can show p-type thermopower. Mott and Davis [8] and Geballe and Hull [9] have pointed out that in semiconducting samples when the carrier compensation ratio $K(=N_A/N_D)$ for n-type material is less than 0.5 the sample may show this type of anomalous thermopower.

It is an established fact [5, 10, 11] that in polycrystalline semiconducting samples, an oxygen chemisorption/desorption mechanism plays an important role in controlling the concentrations of acceptor and donor states, N_A and N_D, respectively. In the as-deposited ZnO film, an excess of oxygen is trapped at the surface and grain boundaries of the film, during the process of their pyrolysis in air. These oxygen trap states are known to give rise to surface acceptor states $[O_2^{1-}]$ that contribute to the possible acceptor concentration, N_A. In the as-deposited film, therefore, the carrier compensation ratio is relatively high and probably greater than 0.5. However, in a vacuum heat-treated film, these so-called surface acceptor states, as well as the other similar states from the grain boundary region, are desorbed and this, in turn, raises the donor concentration, N_D. Thus the compensation ratio, K, is lowered. During this process the chemisorbed O_2^{1-} ion donates one electron to ZnO $[O_2^{1-} \rightarrow O_2 + e$ or $2O^{2-} \rightarrow O_2 + 2e]$ [12], which may either stabilize N_A at the surface, or may neutralize the interstitial Zn^{2+} ions which then can contribute their share to N_D [13]. Thus it is quite likely that the compensation ratio K may be less than 0.5 in the heat-treated film and the sample may show anomalous thermopower.

The carrier concentration, n, of the samples as obtained from the Hall effect is of the order of 3×10^{17} to $\sim 10^{18}\,\mathrm{cm}^{-3}$, and we feel it logical to employ a nondegenerate model to analyse the thermopower data. For a nondegenerate n-type crystalline semiconductor with spherical constant energy surface under thermal equilibrium the thermoelectric power is given by [8]

$$Q = -\frac{K_B}{e}\left(\frac{E_c - E_F}{K_B T} + A\right) \tag{2}$$

where K_B is the Boltzmann constant and E_c is the energy of the conduction band edge; A is a constant that depends on the nature of the scattering process. Normally, for a material like a Fermi glass, A runs between 2 and 4. If energy is measured with respect to the bottom of the conduction band then Equation 2 reduces to

$$Q = -\frac{K_B}{e}\left(A + \frac{E_F}{K_B T}\right) \tag{3}$$

where E_F is the position of Fermi level in the band gap. Harry *et al.* [14] have pointed out that $A = (5/2) - r$, where r corresponds to the scattering index and is equal to -0.5 for piezoelectric scattering and -1.5 for ionized impurity scattering. Thus $A = 3$ for piezoelectric scattering and 4 for ionized impurity scattering. From Equation 2 it is clear that A corresponds to the value of the thermopower at infinite temperature limit.

From Fig. 3 the extrapolated tangent at the higher temperature region of the curves approximately gives a common intercept at the ordinate from which the value of A has been obtained as 3.01. This value corresponds to the scattering index ≈ -0.5 and is an indication that piezoelectric scattering is dominant in these ZnO films. This is in agreement with the fact that ZnO is a piezoelectric crystal [1].

In all our samples it has been found that $E_c - E_F$ varies with temperature, T, and it can be assumed that for a limited temperature range [8]

$$E_c - E_F = E_o - \gamma T \tag{4}$$

where E_o is the low-temperature limit of $E_c - E_F$ and corresponds to the activation energy equivalent to the band gap, and γ is the temperature coefficient of activation energy. Putting Equation 4 into Equation 2

$$Q = -\frac{E_o}{eT} + \left(\frac{\gamma}{e} - \frac{AK_B}{e}\right) \tag{5}$$

Now, the Peltier coefficient, $\pi = QT$, is given by

$$\pi = \frac{E_o}{e} + \left(\frac{\gamma}{e} - \frac{AK_B}{e}\right)T \tag{6}$$

This equation shows that a π versus T plot should yield a straight line and the value of γ can be obtained from its slope. Fig. 5 shows such plots and it is

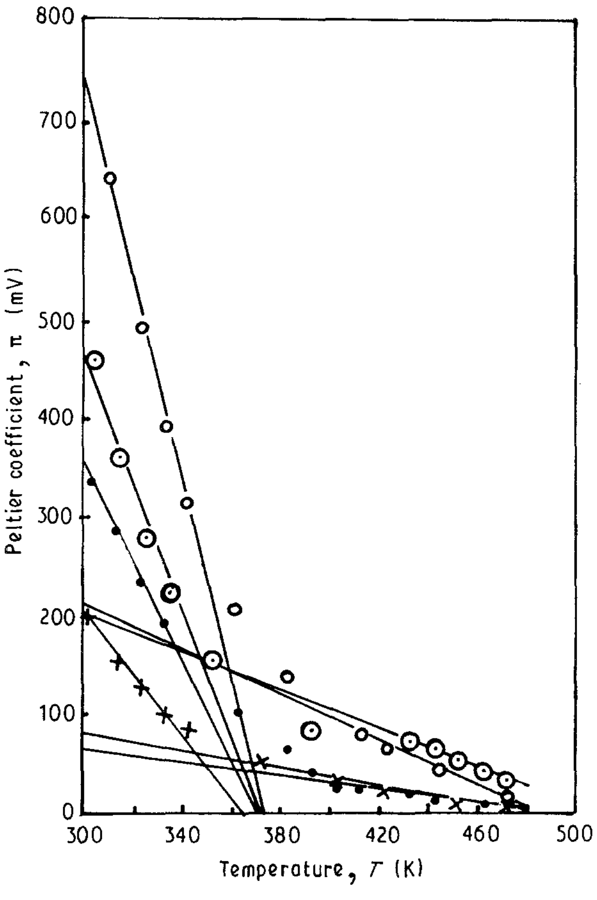

Figure 5 The plot of Peltier coefficient, π, versus temperature, T, of ZnO films of various thicknesses. (○) 205.8 nm, (⊙) 149.1 nm, (●) 131.3 nm, (×) 95.3 nm.

observed that the slopes at room and high-temperature regions are different. Both slopes have been determined and using $A = 3$, various values of γ were calculated for films of different thicknesses. These values of γ are plotted as a function of thickness in Fig. 6. It shows that at high temperatures, γ is almost thickness independent, while in the room-temperature limit, it shows a strong thickness dependence.

Using these values of γ at room temperature, the values of E_0 for the different film thicknesses may be calculated from Equation 6, and the values of $E_c - E_F$ from Equation 4. The variation of E_0 and of $E_c - E_F$ at room temperature as a function of inverse film thickness, $1/t$, is shown in Fig. 7. In this figure it is observed that E_0 has a fair thickness dependence and its bulk value corresponding to $1/t = 0$, is 3.25 eV. This value agrees well with the band gap of ZnO crystal (3.2 and 3.3 eV, respectively) as reported previously [13, 15]. In extrinsic samples, the variation of E_0 with film thickness is obvious. E_0, which is calculated from Equation 4, is some type of thermal activation energy and depends on the detailed variations of the pattern of conduction and valence band edges with the structure of the film, including various defects. This is not necessarily a vertical transition. But the optical band gap, E_g, corresponds to the optical absorption at some frequency and involves mostly vertical transitions between the bands. Thus the variation of E_g with thickness is not so straightforward as for E_0. Of course, carrier concentration plays an important role in this case.

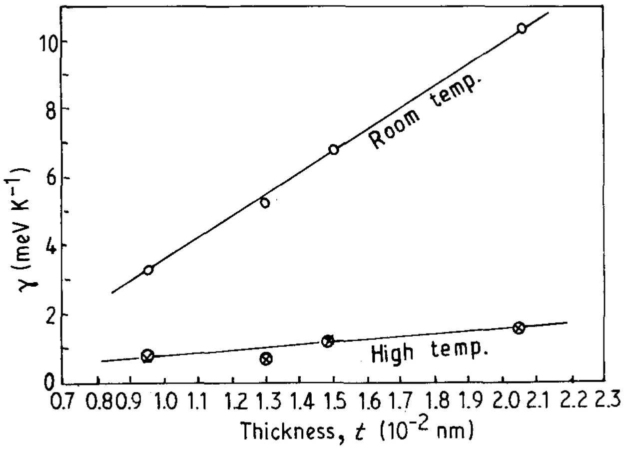

Figure 6 The variation of temperature coefficient of activation energy, γ, as a function of thickness, t, of ZnO thin films at room temperature and at high temperature.

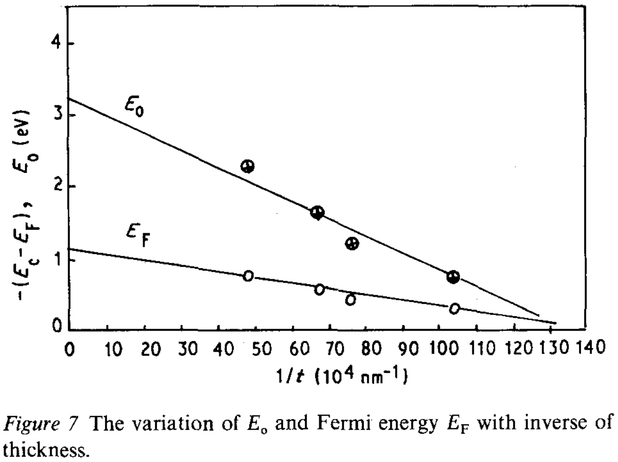

Figure 7 The variation of E_0 and Fermi energy E_F with inverse of thickness.

Because, in the high-temperature region, the thermopower saturates for all the samples (Figs 3 and 4) it suggests that the Fermi levels in these films are pinned near the band edge at higher temperature. This is now shown in Fig. 8 where this pinning can be clearly observed. The gradual decrease of thermopower with temperature as shown in Fig. 3, has also been reported by Hutson [3]. In thin film samples when the material behaves like a Fermi glass, this type of variation is usual [8]. We obtain some idea about this variation by differentiating Equation 2 with respect to temperature, which yields

$$\frac{dQ}{dT} = -\frac{K_B}{e}\left[\frac{d(E_c - E_F)}{K_B T dT} - \frac{(E_c - E_F)}{K_B T^2} + \frac{dA}{dT}\right] \quad (7)$$

From Fig. 8 it is observed that $-(E_c - E_F)$ decreases with temperature so that in the brackets the 1st term of Equation 7 is positive. The second term is also positive because $E_c - E_F$ is negative and we have already ignored any possible temperature variation of A as it corresponds to the high-temperature limit of the thermopower. Thus the whole term in brackets is positive and hence dQ/dT is negative, which suggests a decrease of thermopower with temperature. The minimum value of $-(E_c - E_F)$ as obtained from Fig. 8 is 0.12 eV and is almost five times that of $K_B T$ at room temperature. Thus our previous consideration of a nondegenerate model is justified.

4. Conclusion

Thermopower in spray-deposited nonstoichiometric ZnO thin film shows a thickness as well as temperature dependence. The Fermi levels are found to show a gradual pinning mode near the band edge with increasing temperature. Carrier compensation due to the chemisorption desorption process in these films on annealing in vacuum, may create an anomaly in the nature of the thermopower values. An annealed

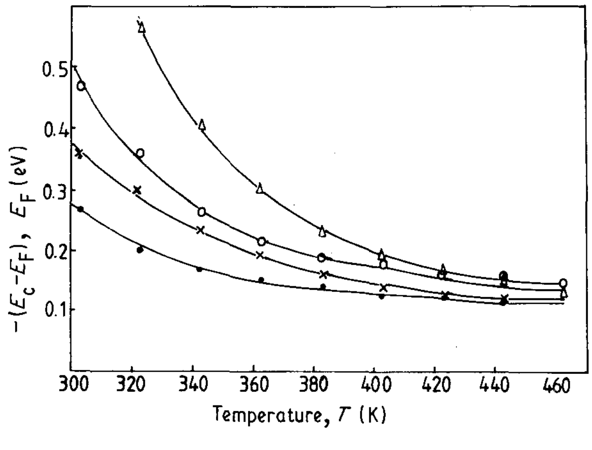

Figure 8 The plot of Fermi level as a function of temperature of ZnO films of different thickness: (△) 205.8 nm, (○) 149.1 nm, (×) 131.3 nm, (●) 95.3 nm.

sample may show a p-type thermopower, while a Hall effect shows n-type behaviour. In general the transport properties in these samples are controlled mainly by the piezoelectric scattering process corresponding to a scattering index of -0.5 obtained from thermopower data. Film thicknesses also have a remarkable effect on the activation energy, E_o, and on the temperature coefficient of activation energy, γ. In the room temperature region, γ has a strong thickness dependence, while in the high-temperature region it is almost thickness independent.

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