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Thermoelectric power of tellurium thin films and its thickness and temperature dependence

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Tellurium thin films of thicknesses between 25 and 200 nm have been vacuum-deposited on glass substrates at room temperature in a vacuum of 5×10^{-5} torr. The thermoelectric power measurements on these films have been carried out, after annealing, in the temperature range from 300 to about 500 K. It is found from the study that thermoelectric power is independent of temperature and is also, apparently, independent of thickness, over the range of temperatures and thicknesses investigated. The results are discussed on the basis of size effect and thermoelectric effect theories.

1. Introduction

A considerable amount of work has been carried out in order to determine the structure and properties of tellurium both in the bulk [1, 2] and in the thin film states (Goswami and co-workers [3–5], Okuyama [6], Okuyama and Kumagain [7], Kubovy and Janda [8–10], Dutton and Muller [11, 12] and others [13–20]) because it is an elemental semiconductor which finds application in thin-film field effect transistors. Goswami and Ojha [3] have shown that Te films, formed at room temperature, have a textured one-degree oriented structure; they measured their resistance, activation energy, mobility, carrier concentration and thermoelectric power in the temperature range 78 to 450 K. They found that the Hall constant, R_H, and the carrier concentration, n, show a maximum and minimum, respectively, between 220 and 280 K which was dependent on film thickness and that the mobility, μ, follows temperature dependence as $T^{3/2}$. The increase of n with decrease of T has been ascribed to the formation of a narrow band due to localized charge impurities. Okuyama [7] has found that the mobility variation with temperature deviates from theory for small-grained thin films due to large grain-boundary scattering and have correlated the deviation with grain size. Mathur *et al.* [17] have studied Cu-doped Te films and found that the addition of Cu decreases the activation energies of mobility and conductivity. They postulate variable range hopping at low temperatures and grain-boundary scattering at high temperatures to explain their results. Capers and White [14] find an exponential dependence of mobility with temperature due to pronounced grain-boundary scattering and have obtained linear dependence of μ with grain size. They have pointed out that defect scattering was also significant and surface scattering was insignificant.

Even though some work has been conducted on the mobility, conductivity and Hall constant variations of Te films, except for the work of Goswami and Ojha [3] and Phahle [13], not much work has been done on the thermoelectric properties of Te films and their thickness dependence. Goswami and Ojha [3] have measured the thermal electromotive force (e.m.f.) of thick Te films (200 to 400 nm) at low temperatures and have found that the thermoelectric power, S, increases with temperature. Above room temperature, data are insufficient and appear to show saturation behaviour. Also, apparently, S, decreases with thickness, but again data are insufficient. The work by Phahle has also been conducted on thick (about 900 nm) films.

In the present study, the thermal e.m.f. of Te thin films of thicknesses in the range 25 to 200 nm have been studied at higher temperatures (above room temperature) to establish whether S is in-

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dependent of temperature and to find the thickness dependence, if any. As Capers and White [14] have shown that surface scattering is insignificant, we would expect to observe a thickness independent thermal e.m.f. in Te thin films.

2. Experimental procedure

Tellurium thin films of thicknesses in the range 25 to 200 nm were vacuum-deposited onto cleaned glass substrates held at room temperature in a vacuum of better than 5×10^{-5} torr at a constant deposition rate ($1.0\,\mathrm{nm\,sec^{-1}}$). The film dimensions were 0.7 cm x 6.5 cm. Each of the films was deposited in an individual evaporation. The film thickness and deposition rate were measured and monitored using a quartz-crystal thickness monitor. After formation, the films were annealed at a temperature of 463 K for about 45 min and were mounted on the thermoelectric power measurement set-up. One end of the film was clamped to a massive copper block while the other end could be heated using a mini-heater clamped to that end. The chamber enclosing the experimental set-up was evacuated to a vacuum of better than 5×10^{-5} torr before the thermoelectric measurements were made. The temperatures of the two ends were recorded using copper–constantan thermocouples. Using the copper leads, the thermal e.m.f. developed across the Te film was measured as a function of the temperature difference between the hot and cold ends using a microvoltmeter in the low temperature-difference range and a digital millivoltmeter in the high temperature-difference range. The cold end of the film had practically a constant temperature 300.5 ± 0.5 K; the hot end of the film had a maximum temperature of 453 K.

3. Results

Fig. 1a and b shows the plots of thermal e.m.f. against temperature difference between the ends of the films. It is seen from the figures that the e.m.f., E, varies practically linearly with temperature difference, ΔT, nearly satisfying the relationship $E = S\Delta T$; the thermal e.m.f. values are found to be reproducible during cooling and heating. Fig. 2 shows the plots of thermoelectric power, defined by $S = E/\Delta T$, as a function of the reciprocal of the absolute temperature. It is seen from Fig. 2 that the thermoelectric power is independent of temperature in the range of temperatures studied (300 to 500 K), within experimental error (about ±2%). Fig. 3 shows the plot of thermoelectric power against thickness for different films. It is observed from Fig. 3 that there is no systematic variation of thermoelectric power with thickness, even though it appears that for thicknesses below 100 nm there is a tendency for it to increase with thickness. Essentially, therefore, thermoelectric

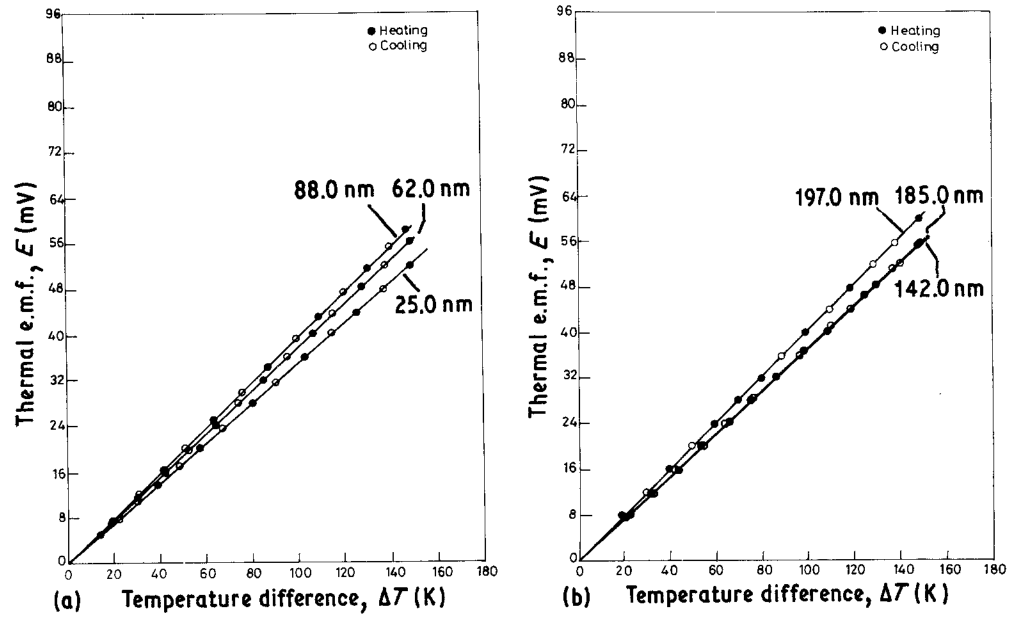

Figure 1 (a) and (b) Thermal e.m.f. against temperature difference plots for tellurium thin films of different thicknesses (25 to 200 nm).

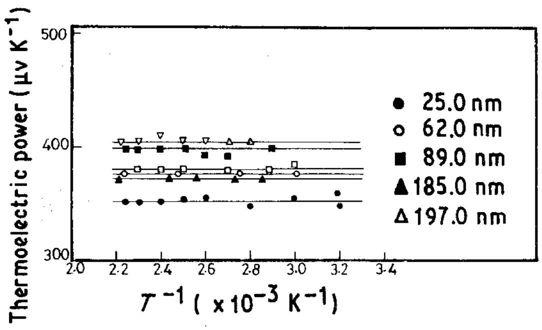

Figure 2 Thermoelectric power, S, against T^{-1} plots for tellurium films of different thicknesses (as used in Fig. 1).

power is independent of thickness. From the sign of the thermal e.m.f. developed it was found that all the tellurium films were p-type.

4. Discussion

In the case of a p-type semiconductor obeying Boltzmann statistics, the thermoelectric power, S, is given by [13, 21]

$$\begin{aligned} S &= (k/e)[(\tfrac{5}{2})+p-(E_F-E_V)/kT] \\ &= (k/e)[(\tfrac{5}{2})+p+\ln(N_V/n)], \qquad (1) \end{aligned}$$

where E_F is the Fermi energy, E_V is the energy of the top of the valence band, k is Boltzmann's constant, e is the charge on the electron or hole, T is the absolute temperature, n is the hole concentration and p is defined by

$$\tau(E) = \tau_0 E^p, \qquad (2)$$

where τ, the relaxation time, is considered to be a function of energy and τ_0 is a constant and N_V is the effective density of states in the valence band, given by

$$N_V = 2(2\pi m_h^* kT/h^2)^{3/2}. \qquad (3)$$

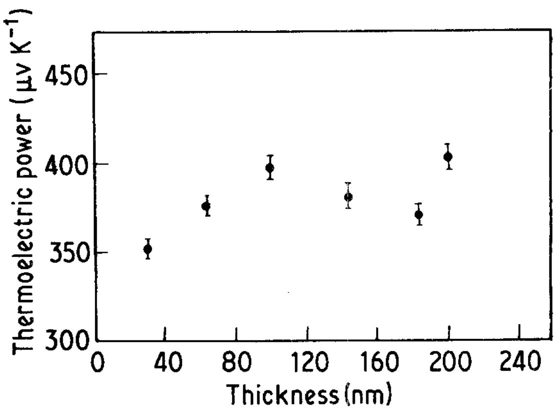

Figure 3 Thermoelectric power, S, against thickness plot for tellurium films of different thicknesses (as used in Fig. 1).

Equation 3 is valid only for $n \ll N_V$, that is, at low temperatures. At higher temperatures, that is, in the impurity depletion region, $n \simeq N_A$ where N_A is the acceptor concentration and $N_V > N_A$ and, hence, S will be constant for a range of temperatures until the intrinsic region is reached, after which point S will begin to increase. Thus, from our experimental results, it can be seen that above room temperature is the impurity depletion region and, hence, S is practically independent of temperature. It should be mentioned that this observation is in accordance with the observation of Phahle [13] for thicker films, who found that S varied as T^{-1} at low temperatures while at high temperatures, above about 250 K, S is independent of temperature. Goswami and Ojha [3] have also found, as mentioned earlier, that S is nearly independent of temperature above 300 K for thicker specimens.

According to classical size effect theory, the thermoelectric power of a thin film is a function of thickness and is given by the relation [20]

$$S_F - S_B = \frac{\pi^2 k^2 T}{3eE_F}[\mathrm{d}\ln(\rho_F/\rho_B)/\mathrm{d}\ln E]_{E_F}, \qquad (4)$$

where S_F and S_B are the thermoelectric powers in the thin film and the bulk state and ρ_F and ρ_B are the corresponding resistivities.

However, ρ_F is a function of thickness, as given by [22]

$$\rho_F/\rho_B = 1+\tfrac{3}{8}\lambda(1-p)/t, \quad \text{for } \frac{t}{\lambda} > 1, \qquad (5)$$

where λ is the bulk mean free path, t is the thickness and p is the specularity parameter, giving the fraction of electrons specularly scattered (without any loss in longitudinal velocity component parallel to the film) from the film surfaces. Therefore, the thermoelectric power of a thin film should also show a thickness dependence.

The present investigation indicates that the thermoelectric power is not a systematic function of thickness in the thickness range 20 to 200 nm, for the temperature range studied, but is apparently independent of thickness. From Equation 5 it can be seen that the ratio ρ_F/ρ_B is a constant, equal to one and independent of thickness, if $p = 1$; hence, S_F will also be independent of thickness if $p = 1$. Thus, it appears that, in the case of the Te films investigated in this work, $p = 1$ and, thus, all the electrons are specularly scattered at the surfaces. This conclusion is justified by the observations of Capers and White [14] which suggest that the surface scattering does not contribute significantly to the transport of charge carriers as the observed mobility was independent of thickness.

5. Conclusions

From the present study of the thermoelectric power measurements of tellurium films of different thicknesses as a function of temperature, it has found that, in the temperature range studied, thermoelectric power is independent of temperature. This has been attributed to the fact that the temperature range corresponds to the impurity depletion region. It has also been found that the thermoelectric power is not a systematic function of thickness and is, apparently, independent of thickness, indicating that the scattering from the surfaces of the film is possibly specular.

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