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Thermoelectric studies on semiconducting Ag_2Te thin films: Temperature and dimensional effects

V. Damodara Das and D. Karunakaran
Thin Film Laboratory, Department of Physics, Indian Institute of Technology, Madras 600 036, India

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Ag_2Te thin films with thicknesses in the range 600—1400 Å have been prepared by vacuum deposition at a pressure of 5×10^{-5} Torr on clean glass substrates held at room temperature. The thermoelectromotive force of these films has been measured in the temperature range 300—415 K, that is, below the phase-transition temperature. It is found that the thermoelectric power of Ag_2Te thin films in the above temperature range exhibits degenerate semiconductor behavior, this is, a linear increase in the thermoelectric power with rising temperature. It is also found that the thermoelectric power obeys the inverse thickness dependence predicted by classical size-effect theories.

INTRODUCTION

The electrical, optical, and structural properties of β-Ag_2Te, the semiconducting low-temperature polymorph of silver telluride stable below about 415 K, have been investigated and reported by several authors.[1–4] Thermoelectric studies, on the other hand, have received much less attention. There have been some thermoelectric studies on bulk samples of silver telluride. Wood *et al.*[5] have measured the Seebeck coefficient of *n*- and *p*-type specimens of polycrystalline Ag_2Te over the temperature range 55—300 K. To understand the carrier-scattering mechansim Aliev *et al.*[6] have studied the thermoelectric properties of bulk Ag_2Te in the temperature range 80—300 K. Astakhov and Golyshev measured the thermoelectric power of polycrystalline stoichiometric specimens of Ag_2Te in the temperature range 88—373 K as a part of their investigation of the kinetic properties of silver chalcogenides. To investigate the phonon drag effect by the carriers of Ag_2Te, Aliev and Nikulin[8] have measured the thermoelectric power of Ag_2Te at very low temperatures, the temperature range being 2—90 K.

It is seen from the above that all the works reported in the literature regarding thermoelectric studies of Ag_2Te are made on bulk samples only. To the best of our knowledge there have been no thermoelectric studies on semiconducting thin films of Ag_2Te. Hence, the present work was carried out. Since the material undergoes a first-order phase transition around 415 K (Refs. 9 and 10) from a semiconducting phase to a metallic phase, we have restricted our observations up to the phase-transition temperature only. The present paper describes the measurement of thermoelectric power of vacuum-evaporated Ag_2Te thin films of thicknesses in the range 600—1400 Å, the temperature range studied being about 300—415 K. The temperature and dimensional effects on the thermoelectric power of β-Ag_2Te thin films are reported and discussed.

EXPERIMENTAL

Thin films of Ag_2Te alloy were prepared by the vacuum deposition of bulk Ag_2Te alloy. The elements Ag and Te used in the preparation of the alloy were of 99.999% purity [Nuclear Fuel Complex, Hyderabad, Department of Atomic Energy (DAE), Government of India] and the usual procedure was adopted in the alloy preparation. That is, the alloy was prepared by melting together Ag and Te in a 2:1 atomic ratio in sealed evacuated quartz tubes. For this, the mixture was heated to a temperature of 1100 °C which is about 100 °C beyond the melting point of the compound and was held at that temperature for about 12 h. Then it was cooled and the compound formed was annealed at 750 °C for several hours and then was slowly cooled further to room temperature. The crystalline phase of the ingot was identified to be β-Ag_2Te (low-temperature orthorhombic phase) by x-ray powder photography. The x-ray diffractograms of the thin-film samples were also taken and they all showed the prominent peaks of β-Ag_2Te thus confirming the structure and alloy formation in the thin-film state. Thin films of Ag_2Te varying in thickness from 600 to 1400 Å were obtained by evaporating bulk Ag_2Te onto cleaned glass substrates, using a molybdenum boat in a vacuum of 5×10^{-5} Torr. The films of different thicknesses were prepared in different individual evaporations. Before evaporation, the glass substrates were cleaned using warm chromic acid, Teepol detergent, and distilled water. They were further cleaned with isopropyl alcohol and mounted inside the deposition chamber. The lateral dimensions of the films were 6.5×1 cm, and the source-to-substrate distance was about 20 cm. The thickness was measured *in situ* using a quartz-crystal monitor and the deposition conditions were maintained almost the same for all the films. The deposition rate was kept constant by allowing the same amount of current to pass through the boat, and each time all the material in the boat was completely evaporated to ensure the composition of the Ag_2Te-alloy thin film formed. Immediately after formation, each of the films was mounted on the thermoelectric power measuring setup one at a time. The chamber enclosing the measurement setup was reevacuated to a vacuum better than 5×10^{-5} Torr and the thermoelectric power measurement was carried out.

The thermoelectric power measurements were made by the integral method, namely keeping one end of the film at a constant temperature and varying the temperature of the other end. The setup used for such a measurement has been described earlier by Damodara Das and Jyotish Chandra Mohanty.[11] The thermoelectric power setup is such that one end of the experimental film can be clamped to a heater attachment and the other end to a massive copper heat sink in order to ensure a constant temperature of that end. It was found that the cold-end temperature was maintained at room temperature, ≈300 K, while the temperature of the other end could be varied from 300 to 500 K. The rise in the cold-end temperature during measurements was less than 1 K above the room temperature.

The temperatures of the hot and cold ends of the film were measured using copper-constantan thermocouples which were fixed to the film mechanically. The thermal emf developed across the Ag_2Te thin film was measured with respect to copper as a function of the hot-end temperature, while the cold-end temperature was constant at about 300 K. The thermal emf's were measured with a high impedance (100 MΩ) digital millivoltmeter.

RESULTS

Figure 1 shows a plot of thermal emf as a function of temperature difference between the hot and cold ends during heating for an Ag_2Te film of thickness 580 Å in the temperature range 300—450 K. It is seen from the figure that the thermal emf increases nonlinearly with an increase in temperature difference up to a certain point (transformation temperature, about 415 K), and then it increases more rapidly at and around the transition point. To analyze the dependence of thermoelectric power on temperature, both in the semiconducting phase and around and above the phase-transition temperature, the thermoelectric power, S_F, of the above film with respect to bulk copper was calculated at different temperatures, and Fig. 2 shows the plot of S_F against temperature. It can be seen from this figure that the thermoelectric power increases linearly with temperature up to the transition temperature, then there is a singularity in the S_F versus T curve at the phase transition. Similar behavior for the temperature dependence of the thermoelectric power during the phase transition has also been observed by Okamoto[12] in the case of Cu_2Se bulk samples. Since our aim was to analyze the effects of thickness and temperature on the thermoelectric power of semiconducting β-Ag_2Te (before the transition occurs), we restricted our subsequent observations to a maximum temperature of about 415 K.

From the sign of the thermal emf developed it was found that all the Ag_2Te thin films were n type as detailed below. A convenient method for the determination of conductivity type in semiconductors is provided by the thermoelectric effect. If contact is made between the semiconductor surface and two metal probes which are held at different temperatures, the sign of the thermoelectric potential difference appearing between the probes will indicate the conductivity type of the semiconductor. Undoped stoichiometric β-Ag_2Te has been reported to be intrinsic and n type,[13] while excess Te (less than about 3 at. % excess) produces β-Ag_2Te which is p type below

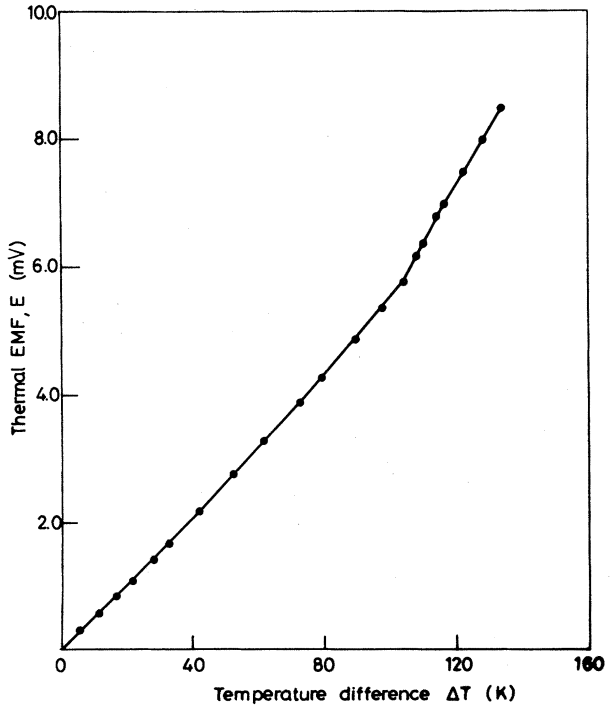

FIG. 1. Thermo emf versus temperature difference between hot and cold ends for an Ag_2Te thin film of thickness 580 Å in the temperature range 300—450 K.

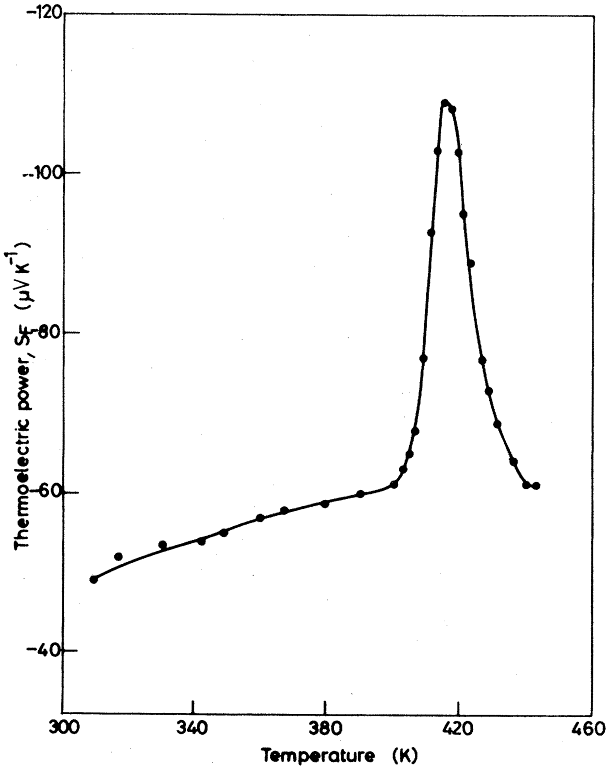

FIG. 2. Thermoelectric power versus temperature for an Ag_2Te thin film of thickness 580 Å in the temperature range 300—450 K.

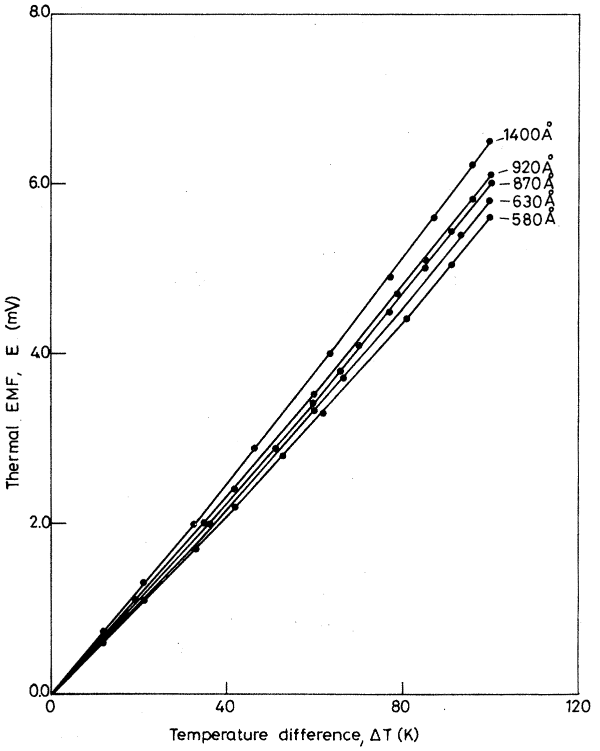

FIG. 3. Thermo emf versus temperature difference between hot and cold ends for Ag_2Te thin films of thicknesses 580, 630, 870, 920, and 1400 Å in the temperature range 300—415 K.

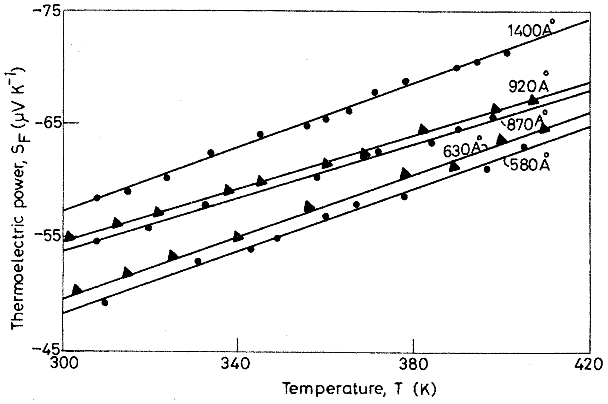

FIG. 4. Thermoelectric power versus temperature for Ag_2Te thin films of different thicknesses.

about 80 K. By increasing the Te content to about 3 at. % excess, the compound can be made *p* type at room temperature, but in this composition range the alloy will be $Ag_{2-x}Te$. In the present work the thermoelectric power S_{AB} of Ag_2Te film (B) with respect to copper (A) was found to be positive and more than 40—50 μV/K (i.e., the hot copper-to-Ag_2Te film junction was positive) indicating that β-Ag_2Te is *n* type. [$S_{AB} = S_A - S_B$ is greater than 0, but $S_A =$ only $+1.7$ μV/K (Refs. 14 and 15), and hence S_B is negative, hence *n* type.]

Figure 3 shows plots of thermal emf versus temperature difference for β-Ag_2Te thin films of different thicknesses in the semiconducting region. Figure 4 shows plots of thermoelectric power S_F versus temperature for films of different thicknesses. It is seen from Fig. 4 that the S_F versus temperature plots for all the films are linear, indicating that S_F is a linear function of temperature.

To analyze dimensional effects, the thermoelectric power was plotted as a function of film thickness at three different temperatures, viz., 300, 340, and 380 K. Figure 5 shows these plots. It is seen that the thermoelectric power of the thinnest film is the lowest (in magnitude) at all the three temperatures, and it increases (in magnitude) rapidly with increasing thickness up to about 1400 Å, and thereafter increases slowly with a further increase in thickness, attaining saturation. It is also seen that the nature of the thickness dependence of the thermoelectric power is similar at the three temperatures. Figure 6 shows the plots of thermoelectric power against reciprocal thickness, at the same three temperatures, and it is seen that all the curves are linear (the points become more scattered about the least-squares fit line, as the temperature approaches about 400 K, which is quite natural because of the onset of phase transition) indicating an inverse functional relationship between S_F and t. The intercept on the Y axis gives the "bulk" thermoelectric power S_B or "grain-boundary thermoelectric power" S_g. S_B is the thermoelectric power of the bulk sample (with very large grain size approximately several micrometers) where the grain-boundary scattering effects are insignificant, while S_g is defined as the thermoelectric power of a bulk sample having the same grain size as the films (grain size approx-

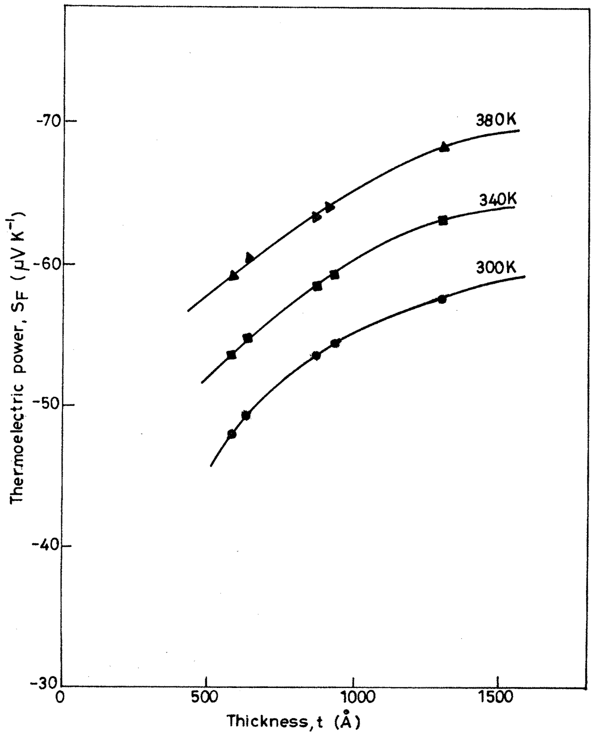

FIG. 5. Thermoelectric power versus film thickness for Ag_2Te thin films at temperatures of 300, 340, and 380 K.

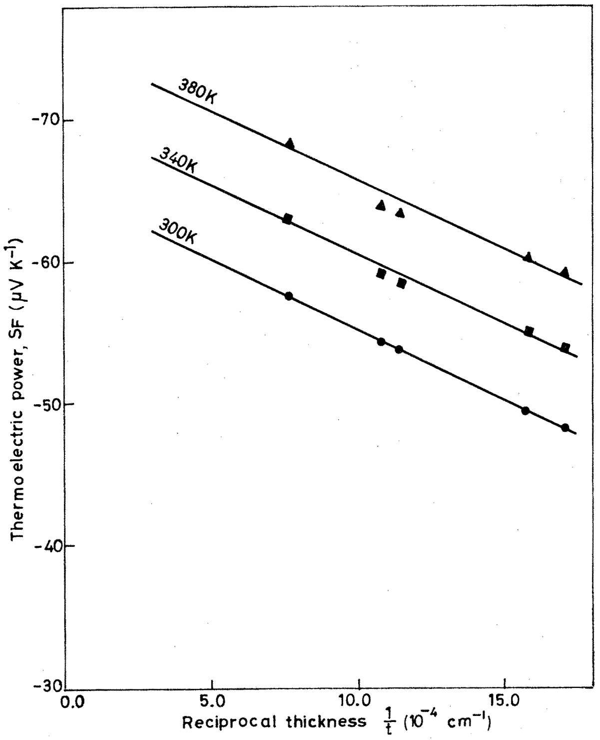

FIG. 6. Thermoelectric power versus reciprocal thickness for Ag_2Te thin films at temperatures of 300, 340, and 380 K.

imately a few hundred angstroms) so that the grain-boundary scattering effects are significant. It is also interesting to note that the slopes of the linear plots of S_F versus $1/t$ at different temperatures are very nearly the same, indicating the near independence of the constant of proportionality between S_F and $1/t$. It can also be noted that the Y intercept shifts to higher (negative) thermoelectric power values at higher temperatures, and the plots at higher temperatures are above those at lower temperatures. This is to be expected because of the increase of thermoelectric power with temperature of all the films.

DISCUSSION

Of all the transport properties, thermoelectric power is the most sensitive to the carrier-scattering mechanism, i.e., the value depends on the mechanism of electron scattering in the transfer of electrons from one portion of the semiconductor to the other. Therefore, the value of S is closely related to the mobility of charge carriers which is governed by the scattering mechanism.

In the free-electron approximation and for a spherical Fermi surface, the thermoelectric power of a metal and/or degenerate semiconductor is given by[16]

$$S_B = \frac{\pi^2 k_B^2 T}{3eE_F}(U+V) , \tag{1}$$

where S_B is the bulk thermoelectric power and $U=(d\ln\lambda_B/d\ln E)_{E=E_F}$, the rate of change of mean free path with the energy evaluated at the Fermi energy, $V=(d\ln A/d\ln E)_{E=E_F}$, the rate of variation of the Fermi-surface area with the energy evaluated at the Fermi energy, e is the charge (in magnitude and sign) of the charge carrier, k_B is the Boltzmann constant, and T is the temperature in K.

Semiconducting β-Ag_2Te is a very narrow band-gap (0.025 eV) semiconductor and has a carrier concentration in the range of temperatures studied equal to about 10^{19} cm^{-3}, regardless of the method of preparation and the purity of the initial components.[17] Also, below 400 K, β-Ag_2Te exhibits a mixed metallic covalent bond nature. Hence, the material behaves as a degenerate semiconductor, and the expression given above for the thermoelectric power should be valid in this case. As the above expression requires a linear dependence of thermoelectric power on temperature, our observation of a linear dependence for S_F on temperature for all the films is in agreement with the above equation. Also Astakhov and Golyshev[7] have investigated the thermo emf of polycrystalline specimens of Ag_2Te, but in the bulk state, in the temperature range 88—373 K, and their results show that the thermoelectric power of β-Ag_2Te increases (in magnitude) linearly with temperature from 273 to 373 K, thus establishing the degenerate behavior of the semiconductor in the temperature range studied.

Taking E_F as $\approx 10^{-2}$ (Ref. 9) and $V=(d\ln A/d\ln E)_{E=E_F}=1$ (i.e., using a spherical Fermi surface as an approximation, since in the literature models for non-spherical Fermi surfaces are unavailable and also that in the absence of the knowledge of the definite value of V the evaluation of U is not possible), it is possible to evaluate the value of $U=(d\ln\lambda_B/d\ln E)_{E=E_F}$, i.e., the energy dependence of the mean free path of the charge carriers, from the slope of S_F versus T plots. Such a calculation gives the value of U as -1.06, so that $\lambda_B \propto E^{-1.06}$ near the Fermi energy.

It is well known that the transport properties of a thin film may be quite different from those of the bulk, particularly if the film thickness is small. This is because as the thickness of the film becomes comparable in magnitude with the electronic mean free path of the material, the film boundaries impose a geometrical limitation on the motion of conduction electrons, and hence on the effective value of the mean free path. Physical effects which appear as a consequence of the reduction of the mean free path due to small dimensions are referred to as classical size effects.

The classical size-effect theory for a free-electron model was worked out by Fuchs[18] for a spherical Fermi surface, and later Sondheimer[19] extended this to include galvanomagnetic effects. Their treatment is a statistical analysis based on the Boltzmann equation for the distribution function of conduction electrons. One of the basic assumptions made in their theory is that the electrons are scattered from the film surfaces either diffusely or specularly, which are the two extreme possibilities to consider. For a sufficiently rough surface the former would apply, and for a mathematically plane surface the latter would be more likely. In the former case, every free path of the electrons is terminated by collision at the surface so that the distribution function of the electrons leaving such a surface is independent of direction. In the latter case, the electrons are elastically scattered from both the surfaces of the film with a reversal of the velocity component normal to the film surface. It is also assumed that a portion, p, of the incident electrons is specularly scattered and the remainder diffusely scattered. The relaxation process for surface scattering is taken to be essentially that for the bulk scattering.

According to the classical size-effect theory mentioned above, the thermoelectric power S_F of a thin film of thickness t is given by[20]

$$S_F=S_B\left[1-\frac{3}{8}(1-p)\frac{U}{1+U}\frac{\lambda_B}{t}\right], \qquad (2)$$

where p is the specularity parameter, giving the fraction of the electrons specularly scattered from the surfaces.

The above expression is valid for monocrystalline films as it does not take into account the contribution to the thermoelectric power due to grain-boundary scattering. Taking into account the effect of grain-boundary scattering along with the background scattering, Pichard *et al.*[21] have derived an expression for the thermoelectric power of a polycrystalline thin film as

$$S_F=\frac{\pi^2k_B^2T}{3eE_F}\left[V+U\frac{\sigma_g}{\sigma_B}-\frac{3}{8}(1-p)\frac{\lambda_B}{t}U\left[\frac{\sigma_g}{\sigma_B}\right]^2\right], \qquad (3)$$

where σ_g and σ_B are the grain-boundary conductivity and the bulk conductivity, respectively, and e is the charge on the carrier in magnitude and sign.

It is seen from the above two equations that S_F is a linear function of reciprocal thickness, if p is assumed to be a constant in both cases. Hence, a plot of S_F versus $1/t$ will be a straight line in either case. However, the intercept on the Y axis gives the bulk thermoelectric power, S_B, or the grain-boundary thermoelectric power, S_g, which is the thermoelectric power of a bulk specimen having the same microstructure (grain size and distribution) as the films, according to the above two equations, respectively. Further, the slopes of the plots of S_F versus $1/t$ contain different parameters according to the two equations [additional parameters according to Eq. (3)]. Thus the nature of the two equations is the same except for the difference in the constant parameters involved in the functional relationship.

The value of S_B or S_g obtained from the slope of the S_F versus $1/t$ plot is -65 μV/K at 300 K. The value reported earlier for bulk samples of β-Ag_2Te is about -120 μV/K.[7] The large difference between the thermoelectric power value obtained by us in the case of thin films and that reported by Astakhov and Golyshev[7] on the bulk polycrystalline samples can be because of the following two reasons. Firstly, thermoelectric power as with any other transport property exhibits anisotropy. As the crystal structure of β-Ag_2Te is monoclinic and/or orthorhombic, thermoelectric power measured in different crystallographic directions will be different.

Our Ag_2Te thin films are polycrystalline. However, Paparoditis[2] has shown by microscopy that the vacuum-deposited Ag_2Te thin films have a characteristic texture. Hence, our thermoelectric power value measured parallel to the film plane can be different from the value of Astakhov and Golyshev.[7] No measurements made on single-crystal bulk samples are available in the literature to the best of our knowledge for comparison. Secondly, the extrapolation of S_F versus $1/t$ plot gives in reality the thermoelectric power (S_g) of the bulk sample, which has the same microstructure as that of the film, viz., very small (approximately a few hundred to 1000-Å size), and too many grains and not S_B, the true bulk value. As the grain boundaries will participate significantly in the scattering of charge carriers when the grain size is very small, the difference in S_B and S_g is expected and understandable.

In the case of polycrystalline films exhibiting grain-boundary effects, for the evalution of U Eq. (3) can be used provided all the other parameters are known. Even though Eq. (2) holds for monocrystalline films only, we can and have used Eq. (2) for an approximate evaluation of U. This is because Eq. (3) itself is an approximation where the approximation $(\sigma_g/\sigma_B)\approx(\beta_B/\beta_g)$ is made and hence a knowledge of $\sigma_g,\sigma_B,\beta_g,\beta_B$ is required for the evaluation of U (β_B and β_g are the temperature coefficients of resistance in the normal bulk and the bulk with filmlike grains). More importantly, this approximation is valid only for metallic films, while our films are semiconducting where the temperature variation of resistance is not only because of increased scattering of electrons at higher temperatures but also, and much more prominently so, because of the generation of additional carriers at higher temperatures. Hence, it is not possible to use Eq. (3) for the evaluation of U in the case of our semiconducting films because of the absence of the knowledge of the parameters β_g and β_B.

Thus, assuming the validity of Eq. (2), we have evaluated from the slope of the S_F vs $1/t$ plot the value of U assuming $p=0$ (or 1, or any intermediate value between 0 and 1). It is found that the value of U obtained from this agrees with that obtained from Eq. (1) if $p=0.99$. As p the specularity parameter gives the fraction of the electrons specularly scattered (without loss in velocity component parallel to film plane), the fraction of electrons specularly scattered in β-Ag_2Te thin films is nearly 1, indicating that specular scattering is the predominant surface scattering mechanism in β-Ag_2Te films.

CONCLUSIONS

It is found from the present study that the thermoelectric power of β-Ag_2Te thin films in the thickness range 600–1400 Å obeys the inverse thickness dependence predicted by the size-effect theories, and that the thermoelectric power increases (in magnitude) linearly with temperature in the range 300–415 K, exhibiting a degenerate semiconductor behavior. It is also found that the surface scattering is predominantly specular.

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