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Semiconducting behavior of Ag_2Te thin films and the dependence of band gap on thickness

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Thin films of Ag_2Te of various thicknesses in the range 500–1500 Å have been prepared by thermal evaporation of the compound under vacuum on clean glass substrates held at room temperature. The electrical resistance of the films has been measured as a function of temperature during heating, which was carried out immediately after the film formation. The observed exponential decrease of resistance with temperature up to the transition point points to the semiconducting nature of the low temperature polymorph of Ag_2Te. The band gap of the low temperature phase is calculated for various thicknesses of the films and it is found that the band gap is a function of film thickness, increasing with decreasing thickness. The increase in the band gap, which was found to be inversely proportional to the square of the film thickness, is attributed to quantization of electron momentum component normal to film plane.

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INTRODUCTION

There has been considerable interest lately in the electrical properties of β-Ag_2Te, the stable low temperature polymorph of silver telluride. The low temperature β phase of Ag_2Te has an orthorhombic[1] or a monoclinic[2] structure. The phase on the other hand is cubic (fcc)[3] after the transition at 411 K. The structure of the alloy, Ag_2Te, an A^IB^{VI} compound has been studied by Mamedov *et al.*[4] by x-ray diffraction technique. Sharma[5] and Dhere *et al.*[6] have studied this alloy in the thin film state at various temperatures by electron diffraction technique. Electrical properties and phase-transition of Ag_2Te films have also been investigated by some workers.[5–7] Undoped stoichiometric Ag_2Te has been reported to be intrinsic and *n* type.[8] The band-gap values of bulk β-Ag_2Te reported in literature are conflicting. The band gap obtained by measurement of the Hall coefficient and resistivity down to about 60 K were reported by Gottlieb *et al.*[9] and by Wood *et al.*[10] as 0.025 and 0.05 eV. Later Dalven *et al.*[11] reported thermal energy gap at 0 K as (0.064 ± 0.009) eV. Bottger and Meister[12] plotted the logarithm of the Hall coefficient versus $1/T$ from 110 to 225 K and obtained an activation energy of about 0.032 eV assuming intrinsic conduction. Earlier work of Appel[13] reported a value of the room temperature energy gap to be 0.67 eV by analyzing optical properties of thin films. Paparoditis[7] through his measurements of electrical resistance and Hall voltage as functions of temperature on evaporated films reported a value of 0.025 eV. It seemed worthwhile, especially in view of the variation in the reported values of the energy gap, to undertake the task of finding the thermal energy gap in the intrinsic region viz., 300–450 K through the measurement of electrical resistance of evaporated thin films in the thickness range 500–1500 Å as a function of temperature. In the present paper, we describe the observations of the semiconducting behavior of Ag_2Te films in the intrinsic region and the thickness dependence of the band gap and give possible explanations.

EXPERIMENT

Ag and Te of 99.999%-purity were used in the preparation of bulk Ag_2Te alloy. The constituent elements in their stoichiometric proportion (2:1) were melted in an evacuated quartz ampoule and maintained at a temperature of 1100 °C which is about 100 °C beyond the melting point of the compound. The sample was kept at this temperature for about 12 h. Then it was cooled and the compound annealed at 750 °C for several hours and then cooled further slowly to room temperature. In this way, uniform ingot of Ag_2Te was obtained. The formation of the compound was confirmed by taking x-ray powder diffraction patterns of the sample from different regions of the ingot. Ag_2Te alloy thin films of thicknesses between 500–1500 Å were prepared by evaporation of the bulk Ag_2Te alloy onto cleaned glass substrates, using a molybdenum boat in a vacuum of 5×10^{-5} Torr. The glass substrates used for film deposition were cleaned by first immersing them in chromic acid for an hour, cleaning them with detergent solution and distilled water and then drying them. They were further cleaned with isopropyl alcohol and mounted inside the deposition chamber. Thick silver contact films were deposited at the ends of the substrates before they were mounted on the substrate holder inside the deposition chamber. The lateral dimensions of the films were 3×1 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. In order to ensure that the composition of the Ag_2Te alloy thin films formed was that of the starting bulk alloy, films of different thicknesses were deposited individually in separate evaporations by allowing the same current to pass through the boat and by taking known quantities of the bulk alloy and completely evaporating the alloy in the boat in each deposition. The x-ray diffractograms of the films formed were taken and it was found that the prominent diffraction lines of the film and also their relative intensities compared well with those of the bulk ingot,

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thus confirming the formation of Ag_2Te films. The diffractograms also showed that the films tended to have a (010) preferred orientation and hence had a texture. This observation is also in accordance with the results of Paparoditis.[7] The film resistances were measured immediately after their formation as a function of temperature to an accuracy of 0.1% using predeposited thick silver films and pressure contacts using a Wheatstone's network. The films were heated uniformly at a rate of 1 K/min. The temperature of the films was measured using a copper–constantan thermocouple which was placed very close to the film on the substrate surface and almost touching it. All the measurements were made in a vacuum not less than 5×10^{-5} Torr in order to avoid oxidation or adsorption of gases as much as possible.

RESULTS

Figure 1 shows the variation of resistance with temperature for a Ag_2Te film of thickness 730 Å in the entire temperature range studied. It is seen from the figure that the electrical resistance decreases with an increase in temperature up to a certain temperature (transformation temperature) and then it increases sharply with temperature at and around the transition point and then increases linearly with further increase in temperature. Thus, is it seen that up to the transformation temperature, it exhibits a negative temperature coefficient of resistance and then it exhibits a metallic behavior. To analyze the decrease in resistance with increasing temperature below the transition temperature, log R vs $1/T$ plots were drawn for the above film and films of other thicknesses. Figure 2 shows these plots of log R vs $1/T$ for Ag_2Te alloy thin films of thicknesses 480, 570, 730, 1050, and 1460 Å in the low temperature region. The linear plots of log R vs $1/T$ for all the films show that all the films are semiconducting in the above temperature region. Since the material undergoes a phase transition at the transition temperature, the temperature range studied is the highest possible intrinsic range temperature of the specimen. Hence, it is possible to calculate the band gap from the slopes of the plots.

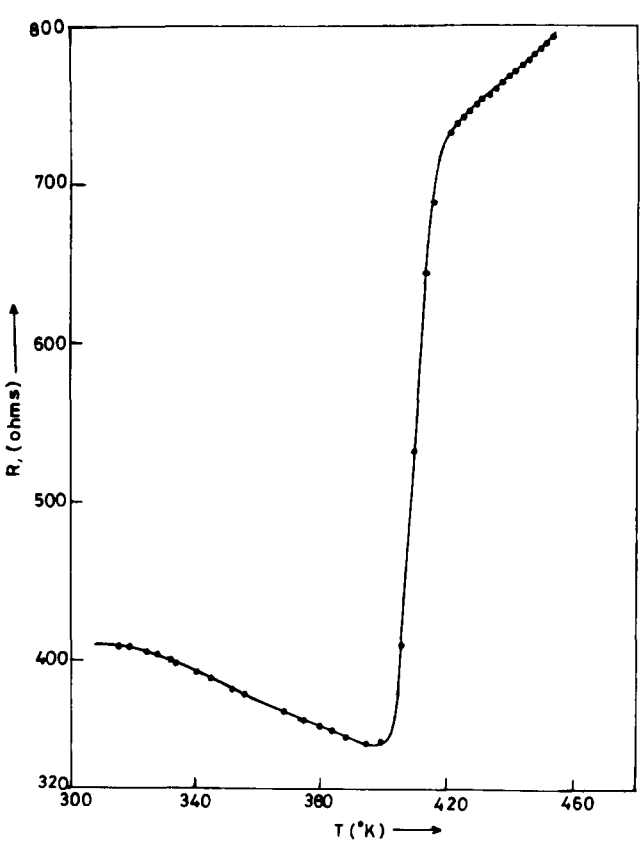

FIG. 1. Resistance vs temperature plot of Ag_2Te thin film of thickness 730 Å in the temperature region 300–450 K showing the phase transition, low temperature semiconducting behavior, and high temperature metallic behavior.

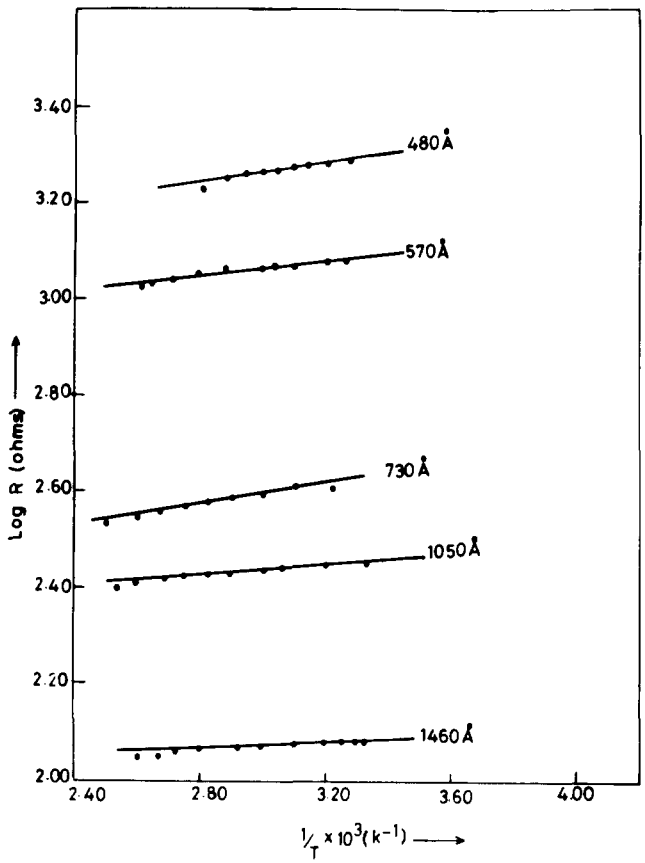

FIG. 2. log R vs $1/T$ plots for Ag_2Te thin films of different thicknesses in the low temperature semiconducting region.

Table I shows the band-gap values for films of different thicknesses and Fig. 3 shows a plot of band gap as a function of thickness. It is seen from these that the band gap varies from 0.087 to 0.016 eV for different film thicknesses, the band gap decreasing with increasing film thickness. Figure 4

TABLE I. Band gap E_g for Ag_2Te thin films of different thicknesses.

Film thickness t (Å)	Band gap E_g (meV)
480	88.0
570	65.5
730	44.5
1050	24.0
1460	16.0

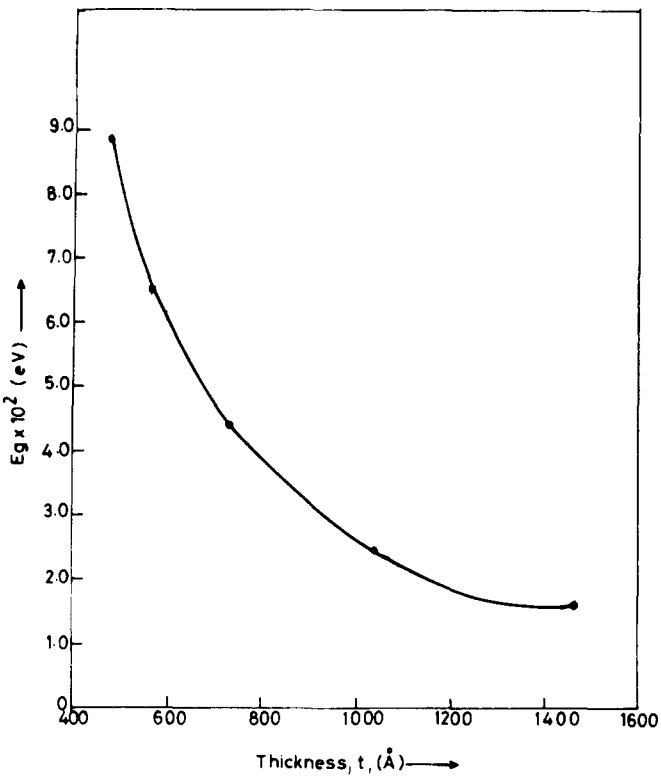

FIG. 3. Band gap E_g as a function of thickness for Ag_2Te thin films of Fig. 2 showing decrease of band gap with increasing thickness.

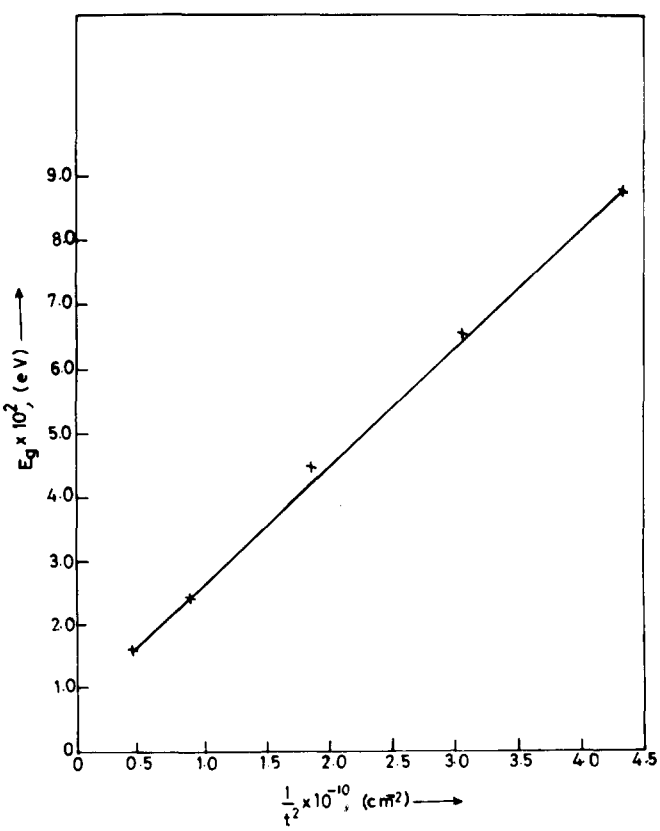

FIG. 4. Band gap E_g vs $1/t^2$ plot showing a linear relationship.

shows a plot of band gap as a function of square of inverse thickness. It is seen that this plot is linear indicating that the band gap varies inversely as square of thickness.

DISCUSSION

The fact that the band gap values observed in the present films are larger than those reported for the same material in the bulk state, and the observation that the band gap is a function of thickness, decreasing with increasing thickness can be due to any one or combined effects of the following causes: (i) the change in the barrier height due to the size of the grains in a polycrystalline film; (ii) a large density of dislocations; and (iii) quantum size effects.

We will see later that the present observations of the dependence of the band gap on thickness can be principally attributed to quantum size effects. We will first consider the first two possibilities. Slater[14] proposed that energy barriers are associated with grain boundaries and their barrier heights can vary because of the charge accumulation at the boundaries. According to him, the increased barrier height is given by

$$E = E_0 + C(X - fD)^2,$$

where E_0 is the original barrier height, C a term depending on the density of charge carriers, electronic charge, and dielectric constant of the material, X is the barrier width of about 200–300 Å, D is the dimension of the grain, and f is a fraction of the order of 1/15 to 1/50 depending on the charge accumulation, and the carrier concentration. It is known from literature[15] that the grain size is approximately proportional to thickness, and hence increases as thickness increases. Hence, if we replace D, the grain size, in the above expression by the film thickness t, we find that E should be proportional to $(X - ft)^2$. However, in the present observations, we find that the band gap varies inversely as the square of the thickness of the film and hence it can be concluded that the observed band-gap variation with thickness cannot be attributed to the above effect.

It is also known that a fairly large number of dislocations are created during the formation of the films and their density increases as the thickness increases up to a particular thickness, beyond which the density is practically constant. However, the dependence of the dislocation density on thickness has not been quantified and in any case the dependence is complex. It has been suggested[16] that when the dislocation density is fairly high as in the case of thin films, there is an increase in the band gap of a semiconductor material, because of the presence of dislocations, provided that the dislocations are separated by a distance greater than the interatomic distance. This separation arises because of the alternate dilation and compression of the lattice on two sides of the dislocation. However, the exact relationship between the dislocation density and/or their separation distance and the change in the band gap has not been established and the magnitude of the separation caused is also unknown. It is however clear that because of the complex nature of the dependence of the dislocation density on thickness and the band gap on dislocation density and the spacing, the variation of band gap with thickness due to the above effect will

be complex. As in the present observation we observe a linear E_g vs $1/t^2$ dependence of the band gap which is expected from the quantum size effect, it is reasonable to disregard the above possibility also.

Sandomirskii[17,18] was the first to consider quantum size effects in semimetallic and semiconducting thin films and to show that when the thickness of a thin film of any material is of the order of de Broglie wavelength of conduction electrons/holes and is much less than the mean free path of the charge carriers, the material exhibits quantum size effects. In the above situation, the electron/hole momentum component normal to the film is quantized and as a consequence the contribution of motion normal to the film to the kinetic energy of the charge carriers is also quantized and is given by

$$E_z = \frac{\hbar^2\pi^2}{2m^*}\frac{1}{t^2}n^2,\ n = 1, 2, 3,...,$$

where $\hbar = h/2\pi$, h is the Planck's constant, m^* is the effective mass of the charge carrier, and t is the thickness of the film. E_z is the kinetic energy contribution due to motion normal to the film plane.

As the lowest momentum-component state is nonzero, the lowest energy state for this motion is also nonzero and hence, the lowest total energy state is also nonzero. As a consequence, the bottom of the conduction band (zero state energy of electrons) and the top of the valence band (zero state energy of holes) in the film state will shift to higher energies with respect to their positions in the bulk state. As a result, if the material is semiconducting in the bulk state, its energy band gap will be increased by an additional amount depending on the thickness of the film. As the increased separation is a function of square of inverse thickness, a plot of band gap versus $1/t^2$ will be linear, as has been observed in the present case. The data available from literature about the effective mass of electrons in Ag_2Te shows that it is small, $\sim 0.05\ m_0$. Also, as the band gaps quoted in literature and observed in the present study are a few tens of meV the Fermi energy is of the order of 10^{-2} eV. Hence, the de Broglie wavelength of electrons in Ag_2Te will be of the order of 1000 Å. It is also reported in literature[9] that Ag_2Te has high mobility (over 10 000 cm^2/V sec at room temperature) and hence has a high mean free path. An estimation of the mean free path from the reported data of electron mobility and effective mass indicate that this is over 2000 Å in the case of Ag_2Te thin films. Hence, the conditions required for the observation of quantum size effect are satisfied in the case of Ag_2Te. Further, the Ag_2Te films tend to exhibit a (010) texture facilitating the observation of quantum size effect. Thus, the increase in band gap of Ag_2Te thin films and its $1/t^2$ dependence observed in the present study can be attributed to the quantum size effect phenomenon. Similar observations of quantum size effect and increased band separation have been made by one of the authors in materials like Bi and BiSb alloys.[19–23] Stasenko[24] has also observed a linear variation of the band gap with $1/t^2$ in CdS thin films. He determined the forbidden energy gap of cadmium sulphide films of various thicknesses from their optical absorption spectra.

From the slope of the band gap versus $1/t^2$ plot, the effective mass of electrons can be calculated using the relation $\hbar^2\pi^2/2m_e^* =$ slope, assuming m_h to be very large, and hence that the band separation is only due to the shift in the conduction band. The value obtained is $0.002m_0$. The de Broglie wavelength of the electrons calculated using the relations $\lambda = h/p, p = \sqrt{2m_e^*E_F}$ (where p is the momentum, m_e^* the effective mass, and E_F the Fermi energy of the electrons) using the value of m_e^* obtained from the slope and taking E_F to be half the band gap of the film of largest thickness is found to be 3000 Å. The assumption made that m_h is very large in the above calculations is reasonable and justified in the light of the fact that as reported in the literature,[7,8,9] the effective mass of holes is larger than that of electrons and the hole mobility is much less than that of electrons, so that the conductivity observed is largely due to electrons and the material Ag_2Te is n-type.

CONCLUSIONS

It is observed from the studies of electrical conductivity as a function of temperature for Ag_2Te thin films of different thicknesses that all the films are semiconducting but with different band gaps below the transition temperature. The band gap is found to be a linear function of inverse square of thickness. These observations can be explained on the basis of quantum size effect and can be attributed to the quantization of momentum component of charge carriers normal to film plane. The effective mass of electrons calculated from the linear plot of E_g vs $1/t^2$ is found to be $0.002m_0$.

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