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Thermal hysteresis during phase transition in Ag_2Te thin films: Thickness effect

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Electrical conductivity and thermoelectric power measurements as a function of temperature have been carried out on Ag_2Te thin films of different thicknesses prepared on glass substrates at room temperature in a vacuum of 5×10^{-5} Torr. It is found that the phase transition temperatures (located by a steep change in resistance and thermoelectric power with temperature) during heating and cooling are different, thereby showing a thermal hysteresis during the phase transition. It is also found that the magnitude of the hysteresis is a function of thickness, increasing with decreasing thickness. This can be due to the large surface-to-volume ratio, small grain size, and a large density of dislocations in thin films.

INTRODUCTION

Compounds of $\text{A}_2\text{B}^{\text{VI}}$ type are attracting increasing attention because of their potential applications in semiconductor technology. The compound Ag_2Te is a narrow-band-gap semiconductor with a high electron mobility ($\mu_n \sim 10\,000 \text{ cm}^2/\text{V s}$ at 300 K) and a low lattice thermal conductivity. It exists in two modifications, a low-temperature monoclinic/orthorhombic modification (β) and a high-temperature (α) cubic (fcc) one. The phase transition, accompanied by a number of characteristic features of the electrical and thermal properties, takes place at $415 \pm 5 \text{ K}$.

Hysteresis is a common feature of both thermal and pressure transitions of the first order. It manifests itself as a difference in the transformation temperatures or pressures in the forward and reverse directions. Some very careful investigations of this phenomenon have been made, from which it appears that when it exists it shows no sign of vanishing in a reasonable period of time and that it is unaffected by the measures which normally assist the establishment of equilibrium.¹

In the literature, some attempts have been made to explain thermal hysteresis in transitions. Schafer² considered thermal hysteresis as arising from the relatively small domain sizes, while Dinichert³ and Frank and Wirtz⁴ explained this on the basis of the different densities of the two phases, causing a strain energy. Thomas and Staveley⁵ have proposed a model based on Turnbull's⁶ theory of nucleation from melts, where the initial growth of the new phase is hindered by the interphase free energy and the strain to which the growing phase is subjected. They have also pointed out that the thermal hysteresis (and the strain energies) may be related to the difference in the volumes of the two phases, ΔV . Based on the principles of elasticity, it has been shown⁷ that the strain energy is a function of ΔV .

Sharma⁸ has studied in detail the structural transformations in Ag_2Te and Ag_2Se thin films by electron diffraction technique. His studies indicate that transformation temperatures during heating and cooling are 430 and 388 K, respectively, in the case of Ag_2Te thin films, and 439 and 380 K in the case of Ag_2Se thin films. On the other hand, x-ray diffraction studies carried out by Mamedov, Gadzhiev, and

Nurieva⁹ on synthesized bulk samples of Ag_2Te reveal that the transition takes place during heating at 420 K and during cooling at 411 K, while the studies¹⁰ on Ag_2Se reveal the transformation temperatures during heating and cooling to be 403 and 394 K.

In the present paper, thermal hysteresis behavior observed during the first-order phase transitions of Ag_2Te thin films by electrical resistance and thermoelectric power measurements is reported and discussed.

EXPERIMENT

Ag_2Te thin films of different thicknesses were prepared by evaporation of Ag_2Te bulk alloy onto cleaned glass substrates, in a vacuum of 5×10^{-5} Torr. To prepare the bulk alloy, Ag and Te of 99.999% purity (Nuclear Fuel Complex, D.A.E., Hyderabad, India) in their stoichiometric proportion (2:1) were melted in an evacuated quartz ampule and maintained at a temperature of 1100 °C, which is about 100 °C beyond the melting point of the compound, for about 12 h. Then it was cooled and annealed at 750 °C for several hours and then cooled further slowly to room temperature. In this way, a uniform ingot of Ag_2Te was obtained. The formation of the compound was confirmed by taking x-ray powder diffraction patterns [Fig. 1(a)] of the sample from different regions of the ingot. The EDAX analyzer attached to a Philips scanning electron microscope was used for the compositional analysis of the bulk Ag_2Te , which also gave a near-stoichiometric composition.

The glass substrates 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 cm \times 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. X-ray diffractograms of the films were taken, and it was found that the prominent dif-

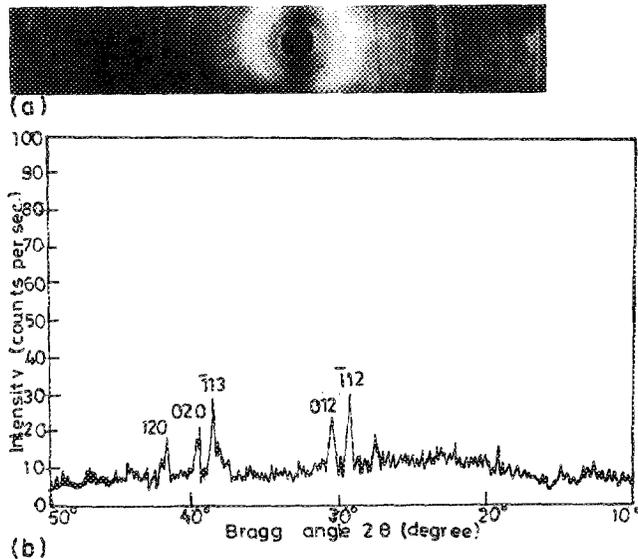


FIG. 1. (a) X-ray powder photograph of the Ag_2Te bulk alloy. (b) Typical x-ray diffractogram of a Ag_2Te thin film.

fraction lines of the film and also their relative intensities compared well with those of the bulk ingot, thus confirming the formation of Ag_2Te films [Fig. 1(b)]. The compositional analysis carried out on as-grown films by a Philips scanning electron microscope attached with an EDAX analyzer also gave a near-stoichiometric composition. Figures 2(a) and 2(b) show the results of the EDAX analysis carried out on the bulk sample and the thin film, respectively. It

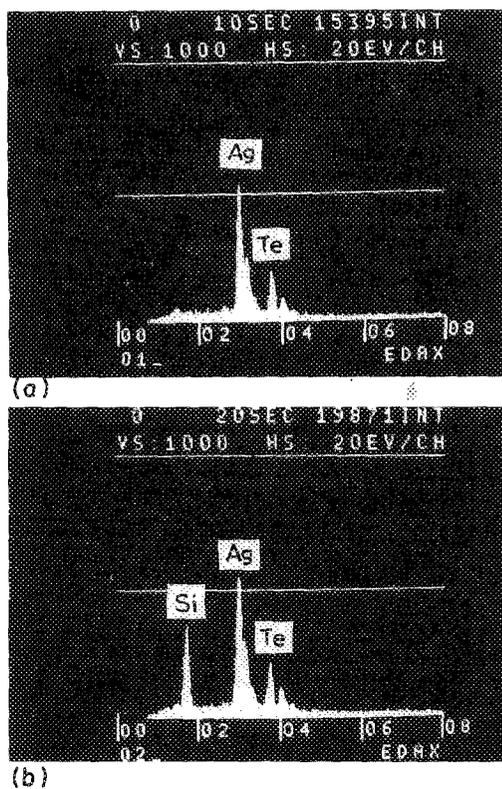


FIG. 2. (a) EDAX spectrum of the Ag_2Te bulk alloy. (b) Typical EDAX spectrum of an Ag_2Te thin film.

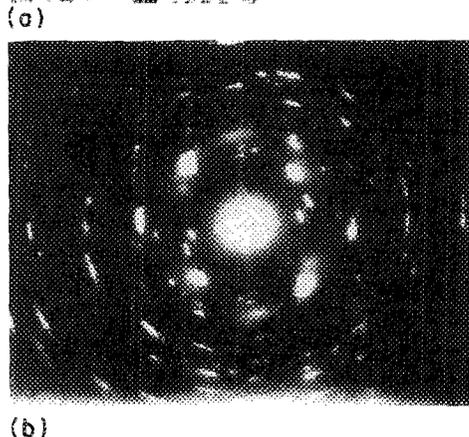


FIG. 3. (a) Transmission electron micrograph of an Ag_2Te thin film. (b) Electron diffraction pattern of the film in (a).

is seen from the figures that the ratio of the peaks corresponding to Ag and Te in the bulk and the thin films is the same, confirming the stoichiometry in the thin films too [the additional peak in Fig. 2(b) of the film is silicon coming from the glass substrate used]. Figures 3(a) and 3(b) show the transmission electron micrograph and selected area diffraction pattern of a typical film grown over rock salt. It is seen from the electron diffraction pattern that the film is polycrystalline, but there is a tendency toward preferred orientation. The film resistances were measured as a function of temperature using a Wheatstone's network. The films were heated uniformly at the rate of 1 K/min. The temperature of the films was measured using a copper Constantan thermocouple which was placed on the substrate surface very close to the film. All the measurements were made in a vacuum of about 5×10^{-5} Torr in order to avoid oxidation or adsorption of gases as much as possible.

RESULTS

Figure 4 shows the typical scanning calorimetric analysis curves of reversible thermal transitions of finely powdered Ag_2Te specimens showing hysteresis. Figure 5(a) shows the plot of electrical resistance as a function of temperature during both heating and cooling for a Ag_2Te film of

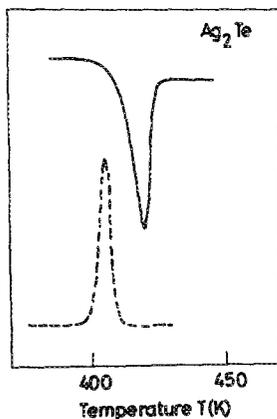


FIG. 4. Differential scanning calorimetric curves of reversible phase transition in powdered specimen of Ag_2Te showing hysteresis.

thickness 820 \AA in the temperature range of about $360\text{--}440 \text{ K}$. It is seen that the phase transition during heating occurs at 429 K , while during cooling at 405 K , thus exhibiting thermal hysteresis of magnitude 16 K . Figures 5(b) and 5(c) show similar plots for the films of thicknesses 590 and 1300 \AA . It is seen from the figures that hysteresis behavior is clearly exhibited by films of all thicknesses and it is worth mentioning that ΔT is found to increase with a decrease of thickness. Also, as observed by Sharma,⁸ the transition temperatures are higher compared to those of the alloys in the bulk state. Figures 6(a)–6(c) show the plots of thermoelectric power as a function of temperature during both heating and cooling for Ag_2Te films of thicknesses 630 , 870 , and 920 \AA in the temperature range of about $300\text{--}440 \text{ K}$. These plots also exhibit the hysteresis behavior.

DISCUSSION

There can be two reasons for the hysteresis. The first one is the formation of a hybrid crystal where both the phases coexist in a small temperature range. Because of the addi-

tional terms involved due to strain and interfacial energies, the hysteresis can appear as suggested by Ubbelohde.¹¹ Alternatively, and more probably, as mentioned in Ref. 12, the hysteresis may arise because the new phase has first to nucleate and then grow, and there will always exist a nucleation barrier whose magnitude will be different for transformations in the opposite directions. In the present case, the high-temperature phase crystal has a larger volume and hence has to be formed in the matrix of the lower volume of the low-temperature phase while heating. This will involve a large strain energy due to compression and hence larger activation energy for nucleation. In the reverse transformation, the crystal of lower volume has to grow in the matrix of the higher volume phase during cooling and hence the strain energy involved will be lowered. The difference in the activation energies needed for nucleation in the two directions will require the transition to occur at different temperatures and hence will give rise to a thermal hysteresis, as observed.

In the present phase transition studies on thin films, as the thickness decreases, the hysteresis range ΔT is found to increase. A physical basis for the large hysteresis range observed in thin films has been given by Parshad and Sharma.¹³ According to them, it is plausible to assume that there is a potential barrier between the atomic arrangements of the two phases. Also, any increase in the anisotropy of interatomic forces or in the interatomic arrangement will make it more difficult for the atomic distribution to change over from one phase to another, thus increasing the barrier height. Because of large surface area-to-volume ratio in thin films, there are appreciable inward forces which are expected to increase the barrier height. Also, the large density of dislocations which is observed to occur in thin films will cause an increase in the anisotropy in the interatomic arrangement, thus increasing the barrier height.

Factors like particle size, rate of heating, and impurities also appear to affect the magnitude of thermal hysteresis. Natarajan, Das, and Rao¹⁴ have investigated particle size effects on thermal hysteresis of the crystal structure transformation of quartz, K_2SO_4 , KNO_3 , NH_4Br , and AgI . The

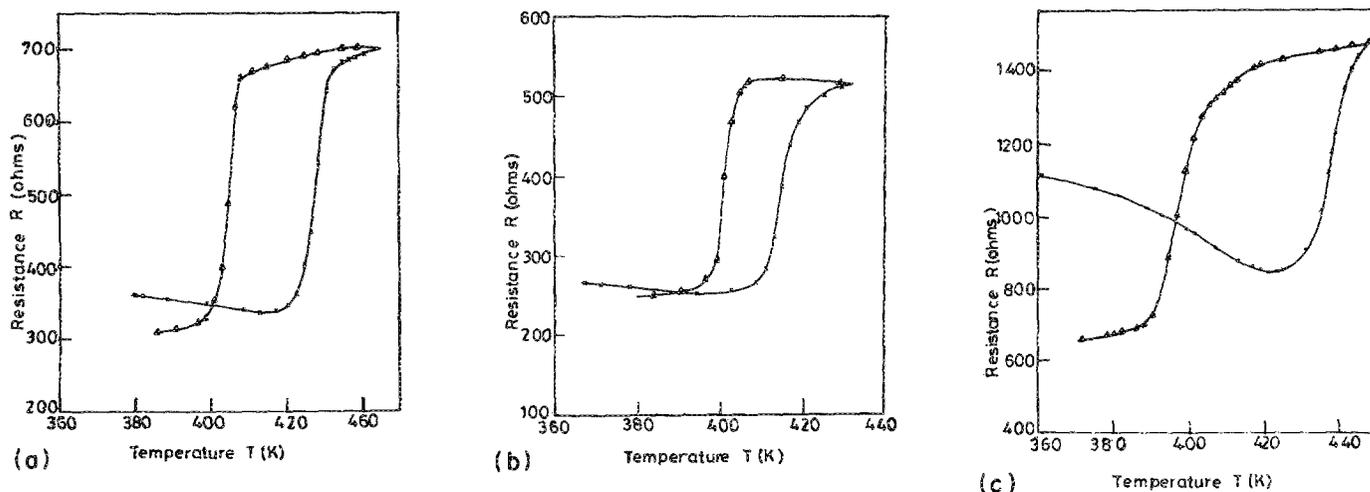


FIG. 5. Resistance vs temperature plots of Ag_2Te thin films of thicknesses (a) 820 , (b) 590 , and (c) 1300 \AA showing thermal hysteresis in phase transition.

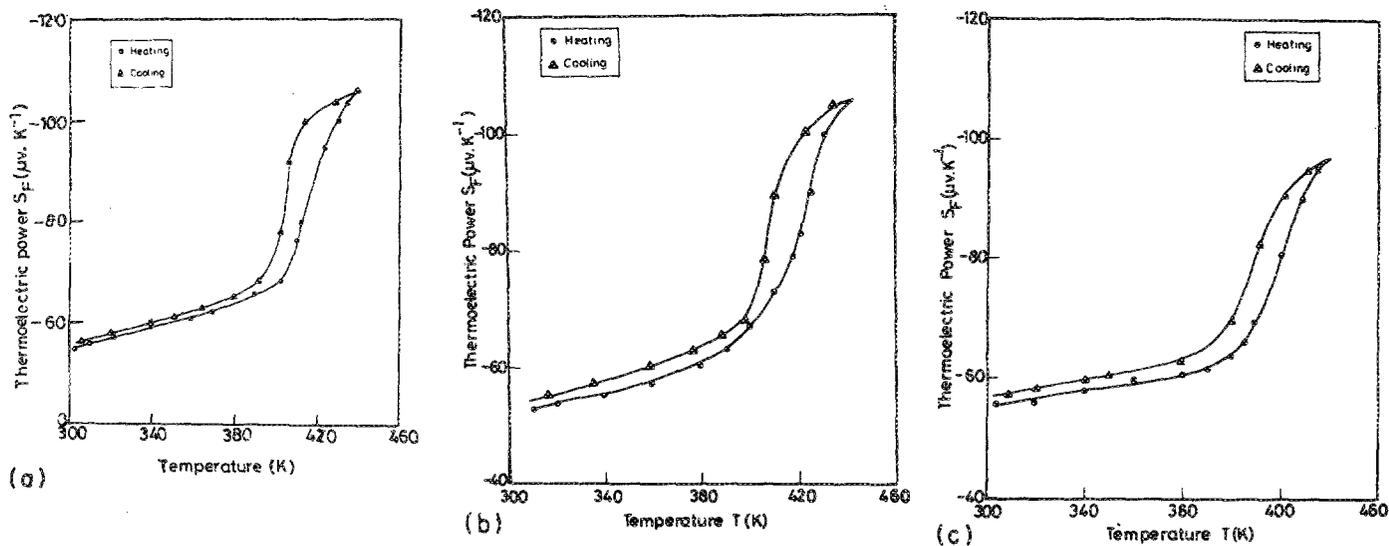


FIG. 6. Thermoelectric power vs temperature plots of Ag_2Te thin films of thicknesses (a) 920, (b) 630, and (c) 870 Å showing thermal hysteresis.

variation of ΔT with particle size is interpreted in terms of Turnbull's⁶ theory of heterogeneous nucleation where the initial growth of the new phase is hindered by the interphase-surface free energy and the strain to which the growing phase is subjected.

Our present studies on Ag_2Te thin films of different thicknesses show clearly that the magnitude of the hysteresis is a function of thickness and increases linearly with decreasing thickness. As is also known, the grain size of a thin film is very small compared to that of the bulk materials and is nearly equal to the film thickness and increases with it. The dislocation density in thin films is also a function of thickness, increasing with it. Further, the surface-to-volume ratio of the film is also a function of thickness, decreasing with increasing thickness. Hence it is reasonable to say that the change in the magnitude of hysteresis observed is due to the combined effects of these causes. However, it is very difficult to estimate the relative contributions of these causes due to the complexity of the dependencies. We feel that the varying and small grain size of the films and changing surface-to-volume ratio as the thickness varies are the main causes for the change in the magnitude of hysteresis observed.

CONCLUSION

The electrical resistance and thermoelectric power measurements carried out on Ag_2Te thin films reveal that these

systems, as observed in the bulk state, undergo first-order reversible phase transitions exhibiting thermal hysteresis. But the hysteresis range observed in thin films is found to be higher than the corresponding bulk materials and a function of thickness. The large surface-to-volume ratio, high dislocation density, and small grain sizes encountered in thin films appear to be jointly responsible for the large and changing hysteresis range observed in thin films.

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