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In situ electrical conductivity and amorphous–crystalline transition in vacuum-deposited thin films of $Se_{20}Te_{80}$ alloy

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In situ electrical conductivity measurements have been carried out on vacuum-deposited thin films of $Se_{20}Te_{80}$ alloy during heating and cooling cycles. The electrical conductivity and X-ray diffraction studies show that the as-grown $Se_{20}Te_{80}$ films are amorphous and, upon heating, undergo an irreversible amorphous-crystalline transition between 315 and 350 K. The observation that the as-grown thin films (deposited at room temperature on glass substrates) are amorphous is in contrast to earlier observations by other workers who find that they are polycrystalline. Above the transition temperature, the electrical conductivity of the polycrystalline $Se_{20}Te_{80}$ films changes as an exponential function of reciprocal temperature. The amorphous–crystalline transition in $Se_{20}Te_{80}$ thin films is broad, with films of high initial resistance having lower transition temperatures and low-resistance films having higher transition temperatures. The observation of a broad transition in the case of the present $Se_{20}Te_{80}$ thin films has to be contrasted with our earlier observations of sharp transitions in the case of $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ thin films.

1. Introduction

Several studies [1–6] made on the behaviour of electrical conductivity in the bulk Se–Te alloy system show how the physical properties of selenium are affected considerably by the addition of tellurium. This is true in the case of thin films also. Although some studies [7–11] have been performed on thin films there is no consistency in the results. We have been interested in the study of thin films of alloys of the Se–Te system to know more about the structural and electrical properties in the thin-film state. This paper describes the behaviour of electrical conductivity as a function of temperature and the amorphous-crystalline transition observed in the as-grown vacuum-deposited amorphous thin films of $Se_{20}Te_{80}$ alloy. We also compare these results with similar studies [12, 13] made by us previously on $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ alloy films.

2. Experimental procedure

Thin films of $Se_{20}Te_{80}$ alloy were prepared by the vacuum deposition of bulk $Se_{20}Te_{80}$ alloy. The bulk polycrystalline alloy used for evaporation was prepared as follows. A stoichiometric mixture (1 : 4) of the respective elements selenium and tellurium of high purity (99.999%) was sealed in an evacuated quartz tube. The quartz tube containing the mixture was heated to a temperature of about 250° C which is slightly above the melting point of selenium and was held at that temperature for 3 days, and around the melting point of tellurium (450° C) for 24 h. Then it was slowly cooled to room temperature. During heating, the tube was frequently shaken to ensure thorough mixing of the alloy. The formation of the bulk polycrystalline $Se_{20}Te_{80}$ alloy was verified by X-ray powder photography. The unit cell dimensions were found to be $c = 0.5726$ nm and $a = 0.4444$ nm, which agree well with the previously reported values [14].

Amorphous films of $Se_{20}Te_{80}$ for the electrical conductivity studies were prepared on glass substrates coated with tin contacts at the ends, kept at room temperature, by the standard vacuum deposition technique. Before the depositions of tin contacts and the experimental alloy film, the glass substrates were cleaned using chromic acid, isopropyl alcohol, detergent solution and distilled water in that order and then dried. Films of different initial resistances were prepared in different individual evaporations. During deposition there is a possibility of preferential evaporation of one of the components (selenium) of the bulk alloy, and the material left over in the boat after an evaporation can have a composition different from that of the bulk alloy. As a consequence, the compositions of the films prepared with the left-over alloy will be different from that of the bulk alloy. In addition, in a given evaporation also, the composition of the bulk alloy can change with respect to time. Therefore, to avoid fractionation of the alloy during evaporation and thereby to ensure the correct average composition of the $Se_{20}Te_{80}$ films formed, for each deposition, a given quantity of the $Se_{20}Te_{80}$ alloy was placed in the boat and the material in the boat was completely evaporated at a fast rate to prepare the

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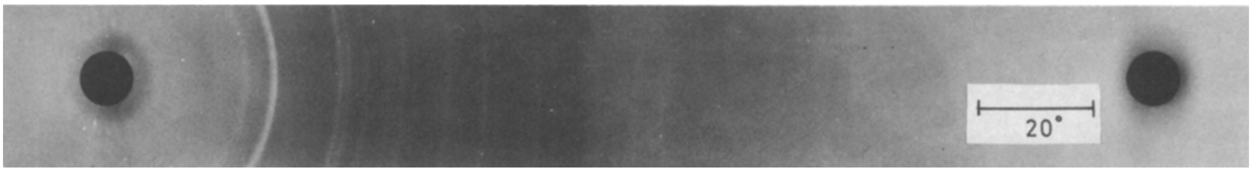


Figure 1 X-ray powder photograph of bulk $Se_{20}Te_{80}$ alloy.

$Se_{20}Te_{80}$ alloy films. The deposition conditions were maintained nearly the same for all the film depositions. The vacuum during each of the depositions and measurements was less than 5×10^{-5} torr.

Soon after the deposition, the electrical resistance of each of the films was measured *in situ* (in a vacuum of 5×10^{-5} torr) as a function of temperature in the range 300 to 430 K for every variation of about 2 K both during heating and cooling. The electrical resistances were measured with a Keithley electrometer to an accuracy of 0.01%. A copper–constantan thermocouple making pressure contact with the glass substrate surface on which the film was deposited was used to sense the temperature of the films. The thermo-e.m.f. was noted on a high-impedance digital millivoltmeter.

Heating of the films above about 450 K caused partial evaporation of the film and so the measurements were made only up to 430 K. To study the change in the structure of the films brought about by the heat treatment, X-ray diffractograms of the $Se_{20}Te_{80}$ films were taken both before and after heating.

3. Results and discussion

Fig. 1 is an X-ray powder photograph showing the polycrystalline nature of the bulk $Se_{20}Te_{80}$ alloy. A comparison of the *d* values calculated from the X-ray powder photograph with the earlier reported values is shown in Table I. The calculated *d* values from the diffraction pattern are found to agree well with the earlier reported values [14], confirming the $Se_{20}Te_{80}$ alloy formation. The X-ray diffractogram of a typical as-grown $Se_{20}Te_{80}$ film is shown in Fig. 2a and that of annealed $Se_{20}Te_{80}$ film in Fig. 2b. The as-grown films are found to be amorphous as there are no peaks in the diffraction pattern, whereas the heat-treated films show prominent peaks of $Se_{20}Te_{80}$ showing the polycrystalline nature of the films after heat treatment. The *d* values of the (1 0 0), (1 0 1) and (1 1 0) peaks noted in Fig. 2b are found to agree with the *d* values of the bulk $Se_{20}Te_{80}$ alloy.

The amorphous nature of the as-grown films of a tellurium-rich alloy like $Se_{20}Te_{80}$ is found to be in contrast to the observations made by previous workers [7, 9] on Se–Te alloy films. Noda *et al.* [7] have reported that $Se_{1-x}Te_x$ alloy films vacuum-deposited

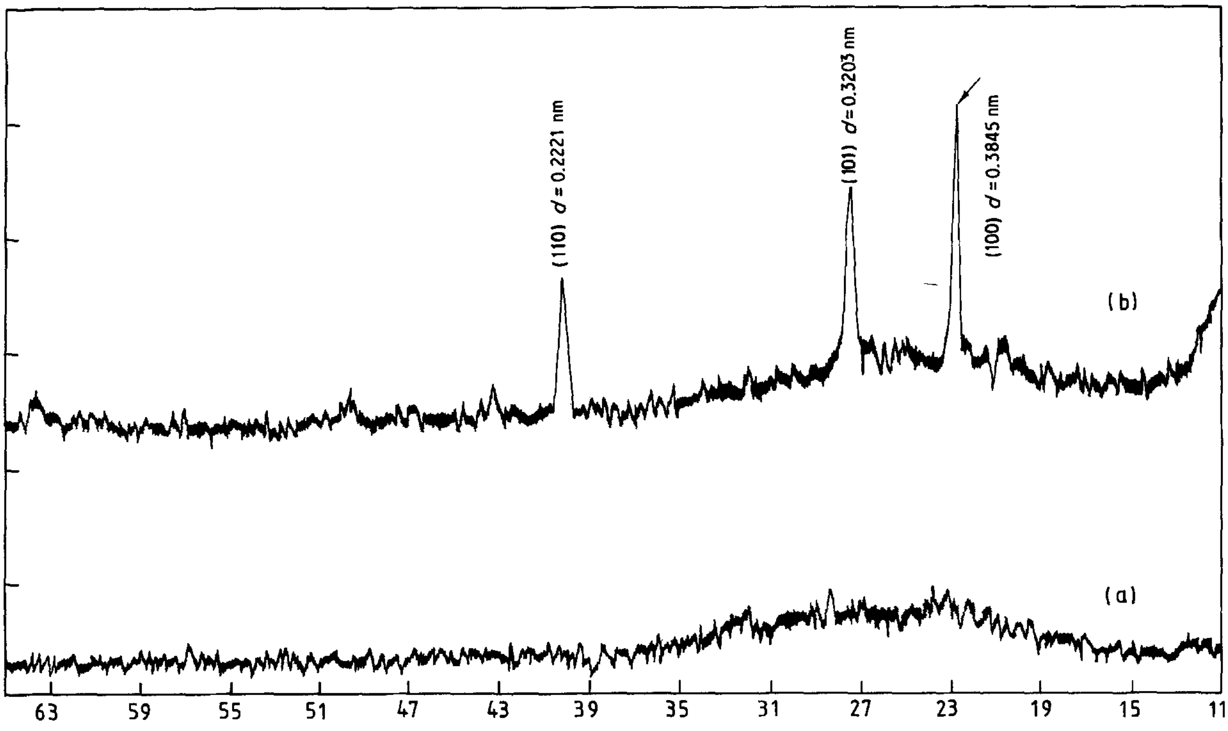


Figure 2 X-ray diffractograms of (a) as-grown and (b) annealed $Se_{20}Te_{80}$ alloy thin films.

TABLE I Comparison of the calculated d values from the X-ray powder photograph with the standard values arrived at from the previous work on bulk $Se_{20}Te_{80}$ alloy [14].

Serial No.	d_{calc} (nm)	$d_{standard}$ (nm)	(hkl)
1	0.3828	0.3849	(1 0 0)
2	0.3133	0.3194	(1 0 1)
3	0.2282	0.2297	(1 0 2)
4	0.2190	0.2222	(1 1 0)
5	0.1906	0.1925	(2 0 0)
6	0.1808	0.1824	(2 0 1)
7	0.1752	0.1755	(1 1 2)
8	0.1591	0.1597	(2 0 2)
9	0.1450	0.1455	(1 2 0)
10	0.1411	0.1410	(1 2 1)
11	0.1293	0.1297	(2 1 2)
12	0.1249	0.1252	(3 0 1)

on to glass substrates held at room temperature become polycrystalline at $x > 0.25$. Watanabe and Kao [9] have observed that vacuum-deposited $Se_{1-x}Te_x$ films with $x < 0.5$ are non-crystalline and that, for films with x between 0.5 and 0.6, the structure is partly crystalline and partly non-crystalline. Our present observation that $Se_{20}Te_{80}$ alloy films vacuum-deposited on glass substrates at room temperature are amorphous is contrary to the above workers' observations, namely that alloy films of tellurium composition only below 25% [7] or 50% [9] are amorphous. Further, our earlier observation of the amorphous nature of $Se_{50}Te_{50}$ alloy films vacuum-deposited at room temperature on glass substrates [13] is also in contrast to their observations but agrees with our

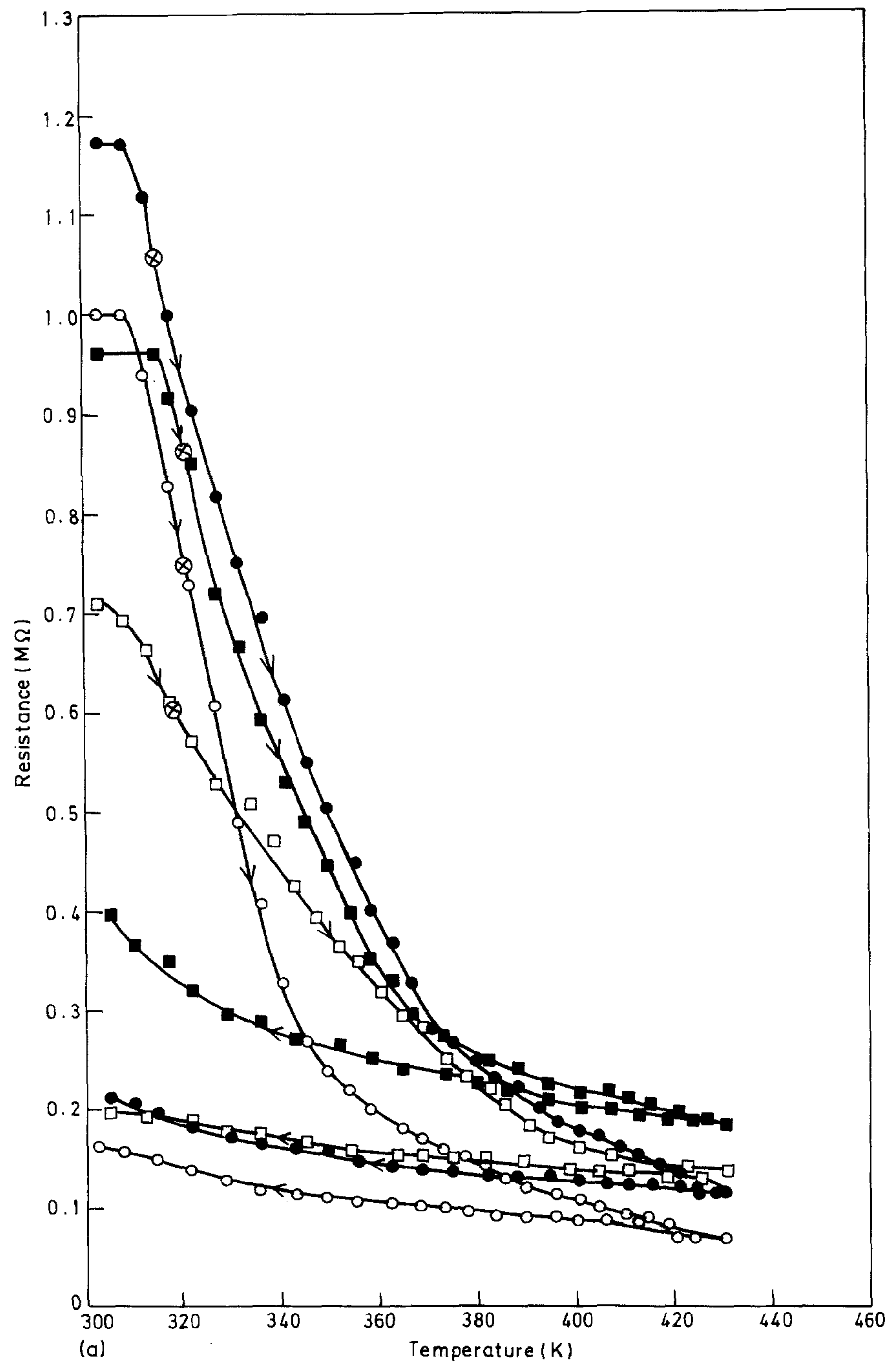
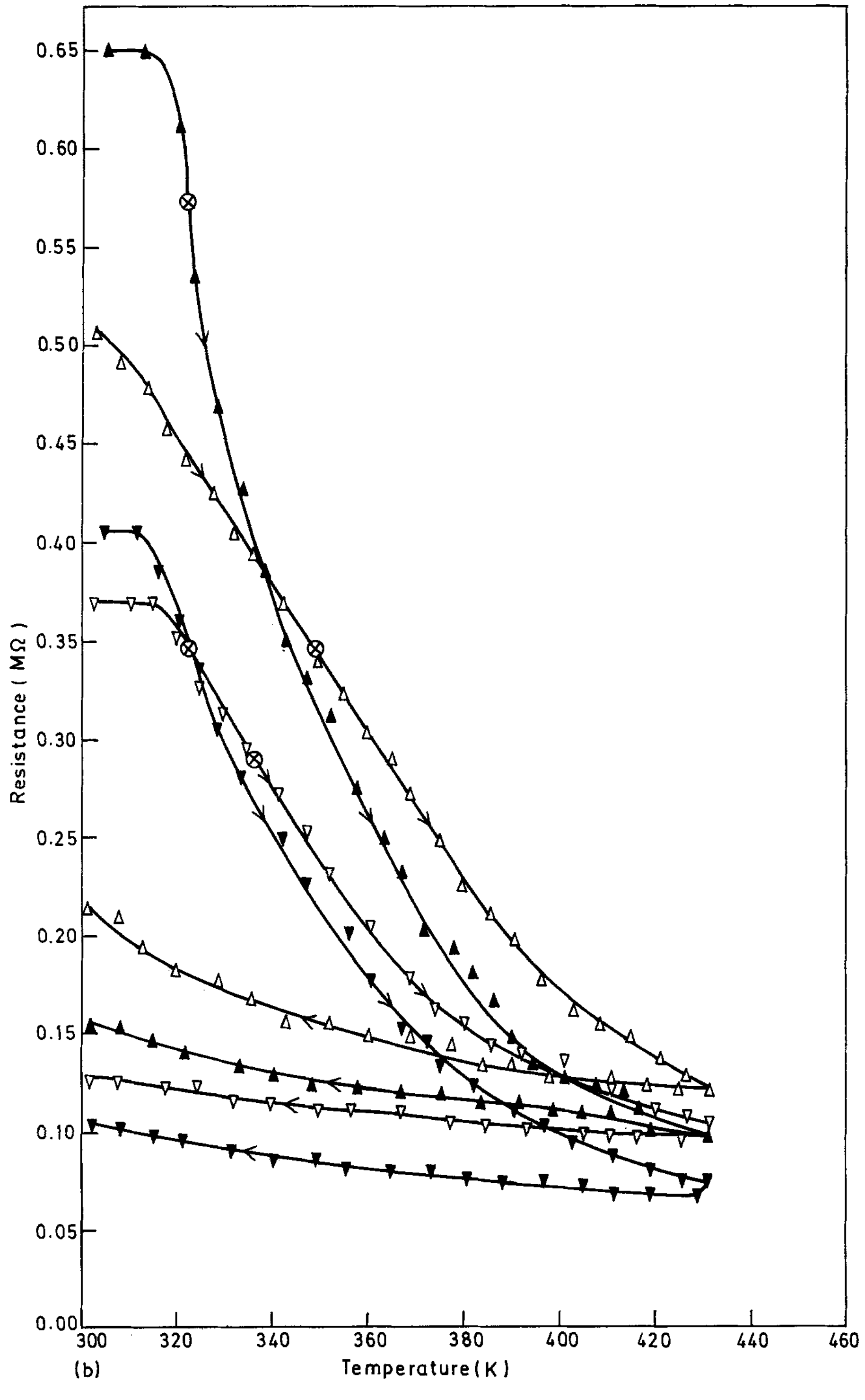


Figure 3 Resistance against temperature plots during heating and cooling of $Se_{20}Te_{80}$ alloy thin films with (a) high initial resistance and (b) low initial resistance; (⊗) denotes the temperature at which the maximum slope occurs.



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present observations on $Se_{20}Te_{80}$ thin films. Lanyon [8] also found that Se–Te alloy films vacuum-deposited at room temperature on glass substrates were amorphous and underwent an amorphous–crystalline transition on prolonged (about 30 to 60 min) heating at around 350 K. Mehra *et al.* [10] have also found that thin films prepared at room temperature even from tellurium-rich alloys like $Se_{20}Te_{80}$ and $Se_{10}Te_{90}$ are amorphous in nature.

Fig. 3 shows the resistance against temperature plots during heating and cooling cycles for the different $Se_{20}Te_{80}$ films. For clarity, the *R–T* plots of high-resistance films are shown in Fig. 3a and those of low-resistance films in Fig. 3b. It can be seen from these plots that the initial resistances of the different $Se_{20}Te_{80}$ films vary between 0.37 and 1.17 MΩ, much less than the initial resistances of amorphous $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ alloy films (varying between 10^8 and 10^{10} Ω) reported by us earlier [12, 13].

From Figs 3a and b it can be seen that during heating there is a rapid (but not sharp) decrease in resistance between 315 and 325 K for the high-resistance films and between 325 and 350 K for the low-resistance films. With a further increase in temperature the resistance decreases much more slowly. During cooling, the resistance increases only slowly with only a small change of about 0.3 MΩ when cooled to room temperature. This nature of the *R–T* plots for all the $Se_{20}Te_{80}$ films implies that an irreversible amorphous–crystalline transition takes place during heating. The transition is not sharp but a broad one in the case of all the films, because, as stated earlier, R–T plots of all the films exhibit a rapid decrease but not a sharp one. This observation is in contrast to our earlier observations on $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ alloy films [12, 13] where we found that the transitions were very sharp except in the case of low-resistance films (thicker films) as the R–T plots showed a sharp, sudden decrease at the transition. In the present case, therefore, we have to define the transition temperature in a particular way to identify a particular temperature as the transition temperature because the transition extends over a range of temperatures. Thus, we define the transition temperature as the temperature where the slope of the R–T plot (during heating) is maximum (i.e. the temperature where the rate of decrease of the resistance with temperature is maximum).

The temperatures where the maximum slope in the R–T plots occurs for the different films are noted in Figs 3a and b by the symbol ⊗ and are between 315 and 325 K for the high-resistance films (Fig. 3a) and between 320 and 350 K for the low-resistance films (Fig. 3b). It is also evident from the figures that even though there is no good systematic variation of the transition temperature with the resistance (thickness) of the films, the high-resistance (thinner) films have lower transition temperatures as compared to low-resistance (thicker) films. It is also evident that the low-resistance (thicker) films have

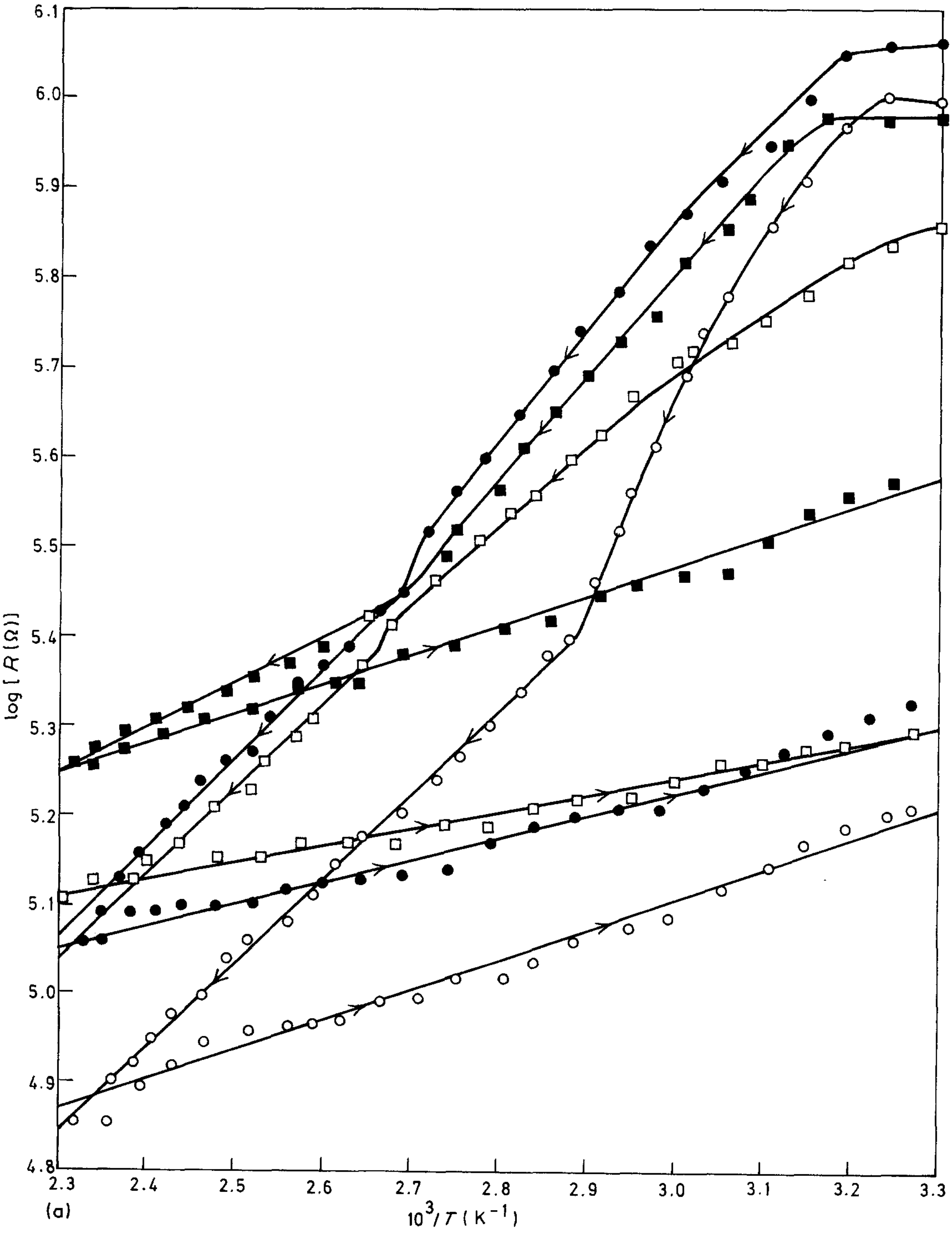

Figure 4 Logarithmic plots of resistance against reciprocal temperature during heating and cooling of $Se_{20}Te_{80}$ alloy thin films with (a) high initial resistance and (b) low initial resistance.

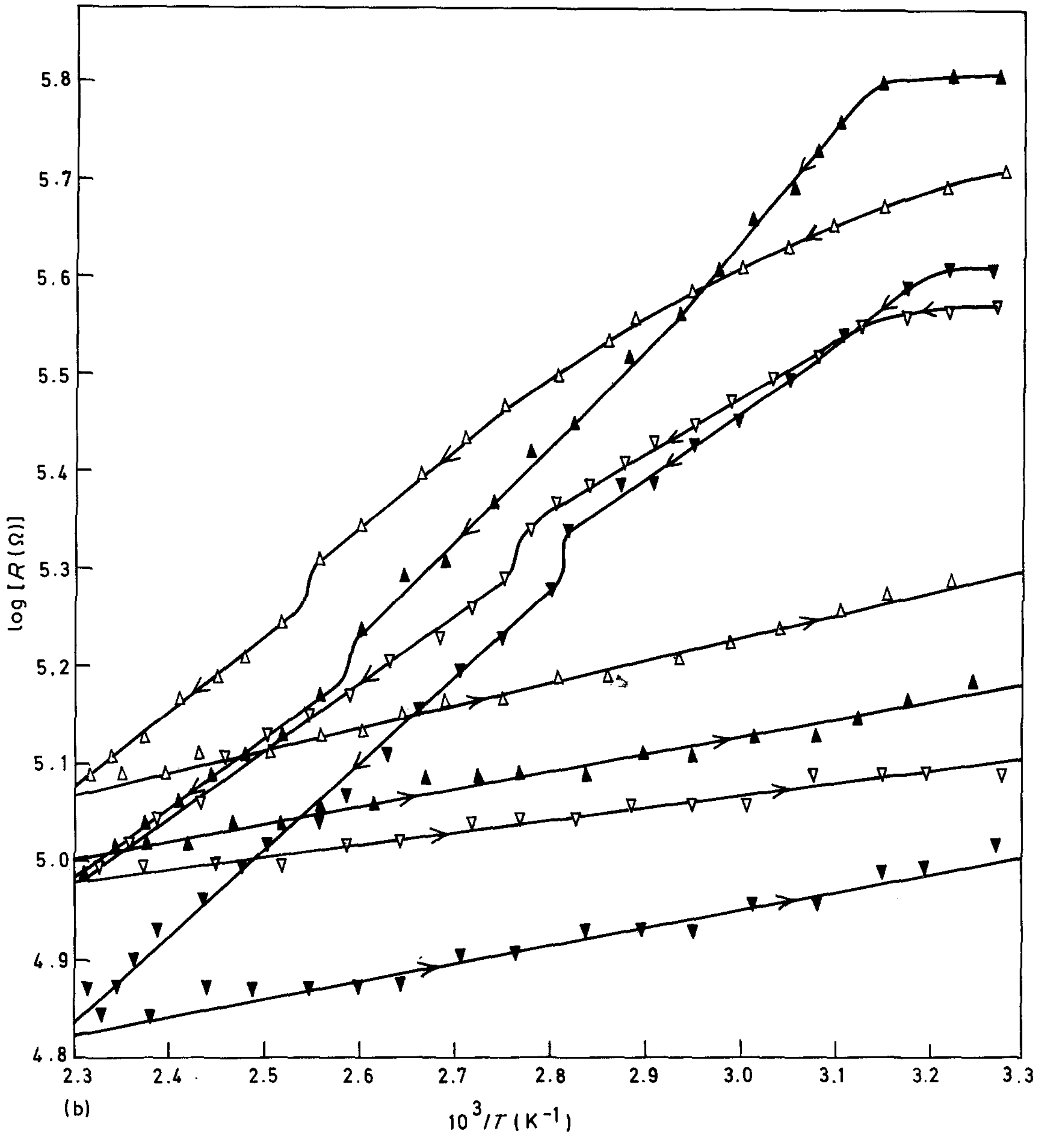

Figure 4 Continued.

broader transitions compared to the high-resistance (thinner) films.

To learn more about the temperature behaviour of resistance of these films, log *R* against 1/*T* plots were drawn and are shown in Figs 4a and b for the high- and low-resistance films, respectively. We find that above the transition temperature (above about 315 to 350 K in different cases) during heating, the log *R* against 1/*T* plots are linear for all the films but with different slopes. During cooling, the plots are linear in the entire temperature range and the activation energies calculated from their slopes are tabulated in Table II. Most of the films have more or less the same slope and their activation energies are seen to vary from about 0.03 to 0.07 eV. From Figs 4a and b we can say also that even below about 320 K during heating the log *R* against 1/*T* plots are linear but with much reduced slopes, indicating probably that the electrical resistance of the films in their amorphous state also varies as an exponential function of reciprocal temperature. However, as experimental points below the transition are very few, this cannot be conclusively said. Conductivity measurements are being carried out below room temperature on these films and will be reported at a later date.

It is interesting to note that kinks occur in the log *R* against 1/*T* plots of all the films as seen from Figs 4a and b. Though the kinks occurring in the case of high-resistance films (Fig. 4a), which are not prominent, appear to be spurious, the kinks for low-resistance films (Fig. 4b) are very marked and pronounced. As

TABLE II Activation energy ΔE for $Se_{20}Te_{80}$ films of different initial resistances as obtained from cooling-cycle conductivity plots (Figs 4a and b)

Initial resistance (MΩ)	Activation energy (eV)
1.17	0.052
1.00	0.062
0.96	0.066
0.71	0.037
0.65	0.035
0.51	0.047
0.41	0.036
0.37	0.027

the kinks occur at temperatures higher than the transition temperature defined and mentioned above (between 315 and 350 K for different films) they do not correspond to the transition temperature (as defined above) but are apparently associated with the end-points of the transition.

X-ray diffraction studies showing the amorphous nature of as-grown films and the polycrystallinity of annealed films support the existence of an irreversible amorphous–crystalline transition in the temperature range 315 to 350 K during the heating cycle.

4. Conclusions

From the electrical conductivity and X-ray diffraction studies made on vacuum-deposited thin films of $Se_{20}Te_{80}$ alloy, it can be concluded that the as-grown films are amorphous and, upon heating, they undergo an irreversible amorphous-crystalline transition between 315 and 350 K. The initial resistances of the as-grown $Se_{20}Te_{80}$ films are of the order of megohms whereas our earlier studies [12, 13] on $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ alloy films show that the films of $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ have much higher initial resistances–of the order of 10^8 to $10^{10}\,\Omega$. The transition in $Se_{20}Te_{80}$ films is broad in contrast to the sharp transitions with an abrupt fall in resistance at the transition temperature, observed in the case of $Se_{80}Te_{20}$ and $Se_{50}Te_{50}$ alloy thin films. Though there does not appear to be any systematic variation of the transition temperature for the different films, it can be said that the high-resistance (thinner) films have a low transition temperature and the low-resistance (thicker) films have a high transition temperature. Above the transition temperature, the electrical conductivity of polycrystalline $Se_{20}Te_{80}$ films varies as an exponential function of reciprocal temperature. Kinks appear in the $\log R$ against $1/T$ plots of all the films during heating and they are apparently associated with the end-points of the transition.

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