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

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The electrical conductivity of thin films of $Se_{80}Te_{20}$ polycrystalline alloy vacuum-deposited at room temperature on glass substrates has been studied during *in situ* heating and cooling cycles. From the electron diffraction of as-grown films it is seen that the studied films are amorphous at room temperature. The electrical conductivity and electron diffraction studies showed that the as-grown amorphous thin films undergo an amorphous–crystalline transition in the temperature range 340 to 360 K. Upon cooling, the films appear to undergo a crystalline–crystalline transition around the same temperatures. There does not appear to be any dependence of the amorphous–crystalline transition temperature on the thickness of the films. However, high-resistance films (thinner films) have a well-defined transition temperature while the low-resistance films (thicker films) have a broader transition. The electrical conductivity of polycrystalline $Se_{80}Te_{20}$ films above 360 K appears to be an exponential function of reciprocal temperature.

1. Introduction

It is known that Se–Te alloys are semiconducting and for some of the selenium-rich compositions the alloy can be formed in the amorphous state. This is also true of thin films of the alloy system. Even so, very little work has been done on thin films of the alloys of the Se–Te system. Mehra *et al.* [1] have studied thin films of the alloys of compositions $Te_{0.90}Se_{0.10}$, $Te_{0.85}Se_{0.15}$ and $Te_{0.80}Se_{0.20}$. They found that the films of all the alloys were amorphous at low temperatures. They also studied the amorphous state electrical conductivity. Okuda *et al.* [2] reported the photocrystallization effect on amorphous $Se_{1-x}Te_x$ films, and Vermaak and Petrwzello [3] studied the amorphous-to-crystalline phase transformation and growth of the Te–Se films. Arrial *et al.* [4] studied the electrical conductivity of $Te_{50-x}Se_{50}Sn_x$ ($3 < x < 10$) thin films and reported that all the compounds showed a sharp transition from an amorphous to crystalline state at a nearly constant temperature. The present work was carried out to study, in more detail, vacuum-deposited thin films of $Se_{80}Te_{20}$ alloy.

2. Experimental procedure

Amorphous $Se_{80}Te_{20}$ alloy thin films were prepared by vacuum deposition of bulk polycrystalline $Se_{80}Te_{20}$ alloy at room temperature at a pressure of 5×10^{-5} torr. The bulk polycrystalline $Se_{80}Te_{20}$ alloy was prepared by heating a stoichiometric mixture of selenium and tellurium of 99.999% purity in a sealed silica tube. The formation of the alloy $Se_{80}Te_{20}$ and its crystallinity were verified by Debye–Scherrer diffraction as shown in Fig. 1. The thin films of $Se_{80}Te_{20}$ alloy were prepared on glass substrates with tin contacts at the ends and, after formation of films in vacuum, the electrical conductivity was measured *in situ* during heating and cooling. Simultaneously, films were also prepared on NaCl substrates held close to glass substrates. The films were also examined by electron microscopy at room temperature both before and after heat treatment and some after heating at 80° C. Electrical resistance measurements were carried out using a Keithley electrometer, to an accuracy of 0.01%.

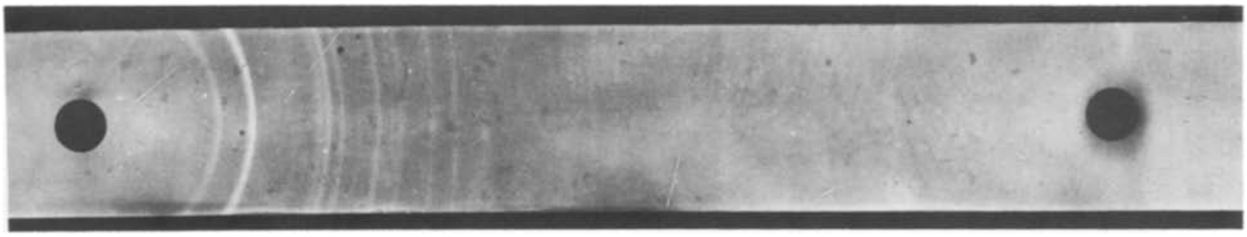

Figure 1 X-ray powder photograph of $Se_{80}Te_{20}$ alloy.

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TABLE I Comparison of the calculated d values from X-ray powder photograph with the standard d values arrived at from the previous work on bulk $Se_{80}Te_{20}$ alloy [5]

No.	d_{calc} (nm)	$d_{standard}$ $Se_{80}Te_{20}$ (nm)	hkl
1	0.3768	0.3804	100
2	0.3012	0.3057	101
3	0.2189	0.2196	110
4	0.2111	0.2128	102
5	0.2009	0.2019	111
6	0.1882	0.1902	200
7	0.1651	0.1669	112
8	0.1522	0.1528	202
9	0.1435	0.1437	210
10	0.1375	0.1384	121

3. Results and discussion

From Fig. 1 it is clear that the bulk alloy formed ($Se_{80}Te_{20}$) is crystalline. The d values calculated from the diffraction pattern, given in Table I, agree with those arrived at from the previous work on bulk alloys [5].

Figs 2a and b show the electron diffraction pattern and the electron micrograph of a typical as-grown (unannealed) film. It is seen from Fig. 2a that the as-grown films are amorphous in nature at room temperature. Fig. 3 shows resistance–temperature plots during heating of the films of different initial resistances. It can be seen that there is a rapid sharp fall in resistance of the films between 340 and 360 K and that with a further increase in temperature the resistance decreases much more slowly. Fig. 4 shows the resistance–temperature variation of the same films while cooling. It can be seen from the cooling curves that resistance does not increase sharply with decreasing temperature, unlike in the case of heating, for all the films. This clearly shows that an irreversible transition has taken place between 340 and 360 K. We postulate that this transition is an amorphous–crystalline one because of the rapid fall in resistance during the transition. In order to verify the amorphous–crystalline transition, the films grown on rock-salt were also subjected to similar heating and cooling cycles and were examined in the electron microscope at room temperature. Figs 5a and b show the electron diffraction pattern and micrograph of a typical heat-cycled film. It is seen from Fig. 5a that the film is no longer amorphous but is polycrystalline. Table II shows a comparison of calculated d values from the grainy ring pattern of Fig. 5a with those of the bulk $Se_{80}Te_{20}$ alloy. It is seen that there is good agreement and hence the film material is $Se_{80}Te_{20}$. Thus, it can be said that the transition taking place between 340 and 360 K is an amorphous–crystalline transition.

TABLE II Comparison of the calculated d values from the ring pattern of Fig. 5a with the standard d values of $Se_{80}Te_{20}$

No.	d_{calc} (nm)	$d_{standard}$ ($Se_{80}Te_{20}$) (nm)	hkl
1	0.3071	0.3057	101
2	0.2570	0.2568	002
3	0.1889	0.1902	200
4	0.1431	0.1437	210
5	0.1275	0.1284	004

To study the electrical conductivity in more detail, logarithmic plots of resistance against reciprocal temperature were plotted and are shown in Fig. 6 during heating and, in Fig. 7 during cooling. It is seen that above 360 K the log R against $1/T$ plots while heating are linear. It is also seen that the high-resistance films exhibit higher slopes of linear log R–$1/T$ curves whereas films of lower resistance show smaller slopes. The activation energies in the two cases are 0.50 ± 0.02 and 0.30 ± 0.01 eV. From Fig. 6 it is also seen that below about 340 K the log R–$1/T$ variation is linear but with much reduced slopes. Thus, it appears that in the amorphous state too, the film resistance behaves exponentially as $1/T$. However, as the measurements were carried out only from room temperature, only a few data points are available below the transition temperature for reaching a definite conclusion about the nature of the conductivity variation in the amorphous state. Further work in the low-temperature region is being carried out to analyse the electrical conductivity of amorphous films and will be reported at a later date.

From R–T plots during the heating cycle (Fig. 3) the transition temperature for different films can be estimated from the temperature of maximum slope. It can be seen that the high-resistance films have a sharp transition temperature while the low-resistance

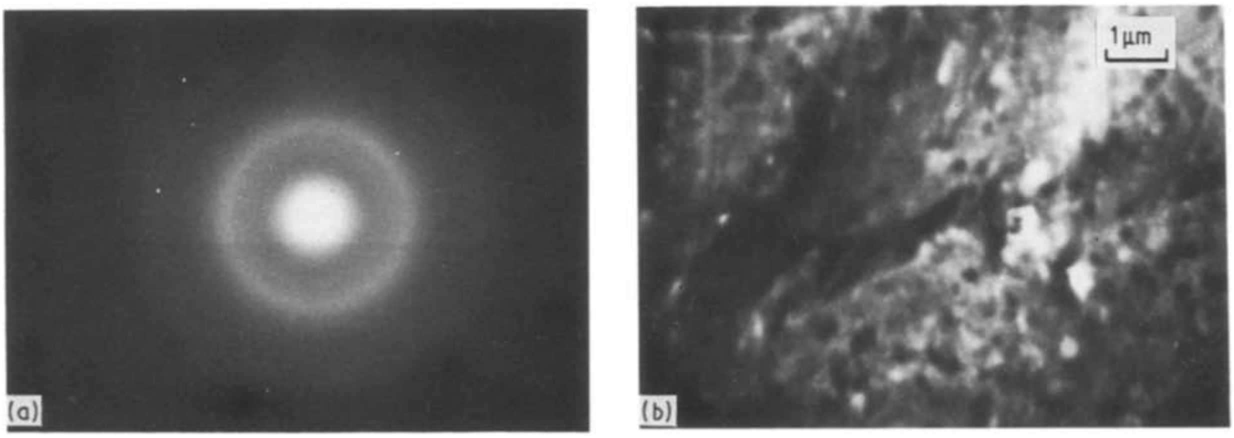

Figure 2 (a) Electron diffraction pattern and (b) electron micrograph of as-grown $Se_{80}Te_{20}$ film.

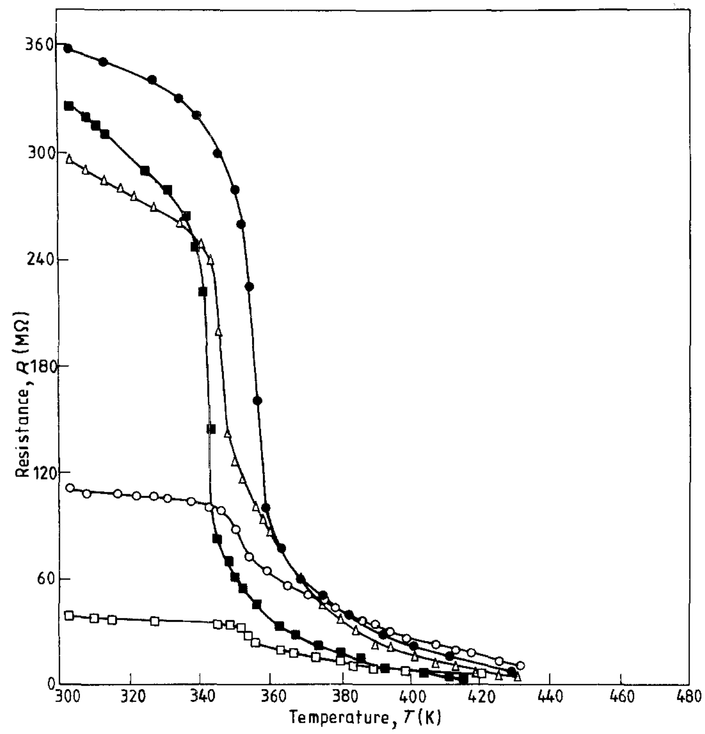

Figure 3 Resistance against temperature plots during heating of $Se_{80}Te_{20}$ alloy thin films.

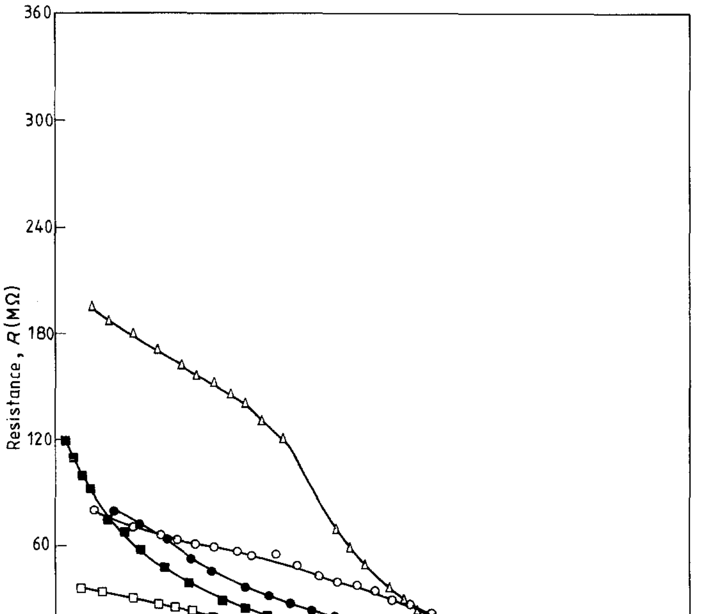

Figure 4 Resistance against temperature plots during cooling of $Se_{80}Te_{20}$ alloy thin films.

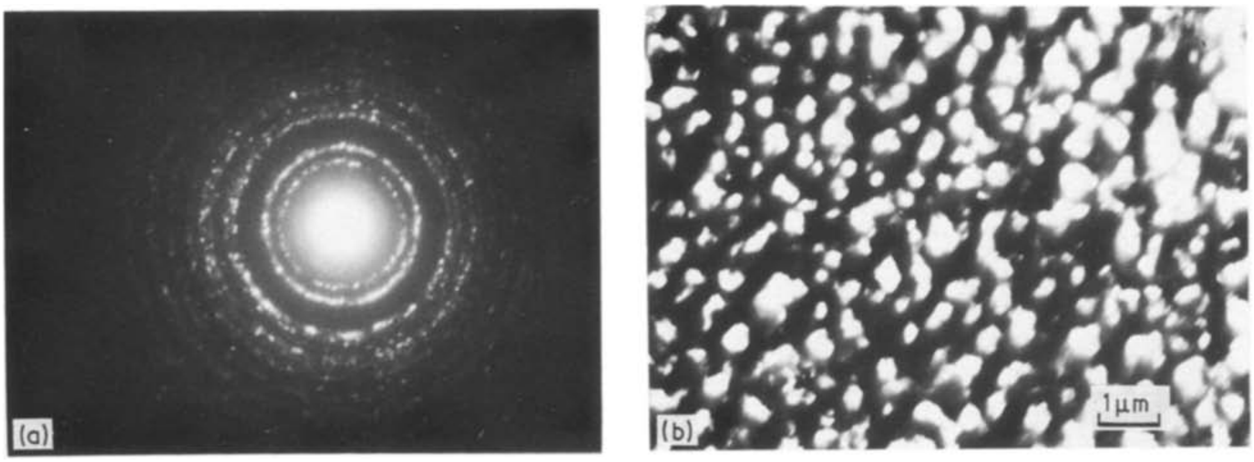

Figure 5 (a) Electron diffraction pattern and (b) electron micrograph of a typical heat-cycled $Se_{80}Te_{20}$ alloy film.

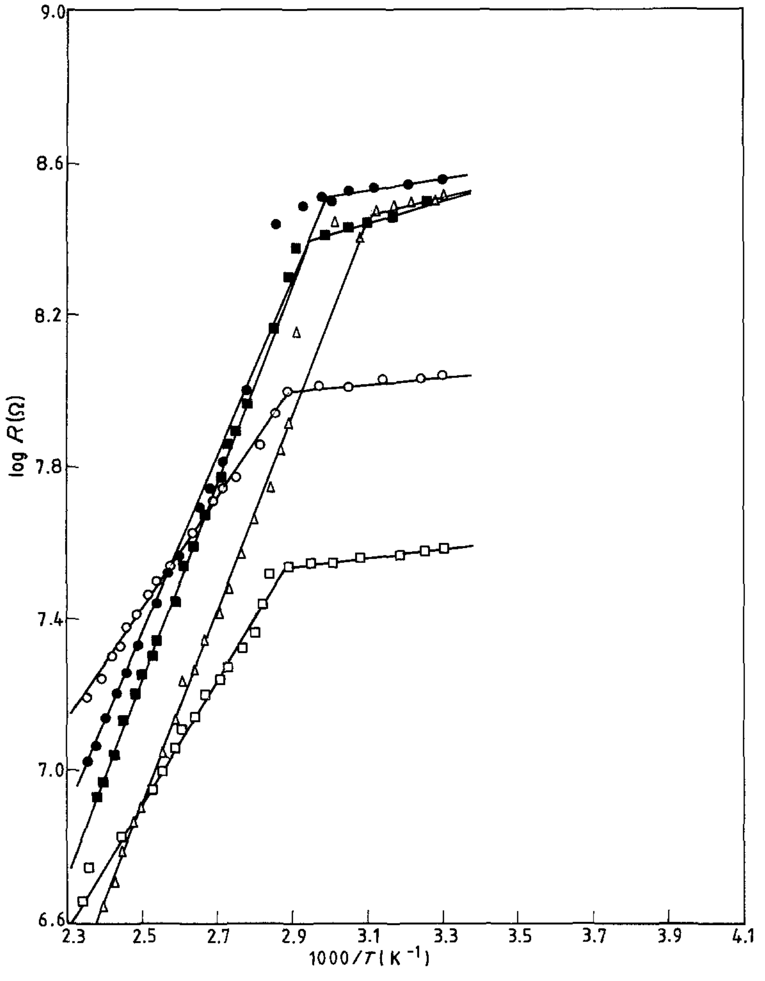

Figure 6 Plot of log R against $1/T$ for $Se_{80}Te_{20}$ films during heating.

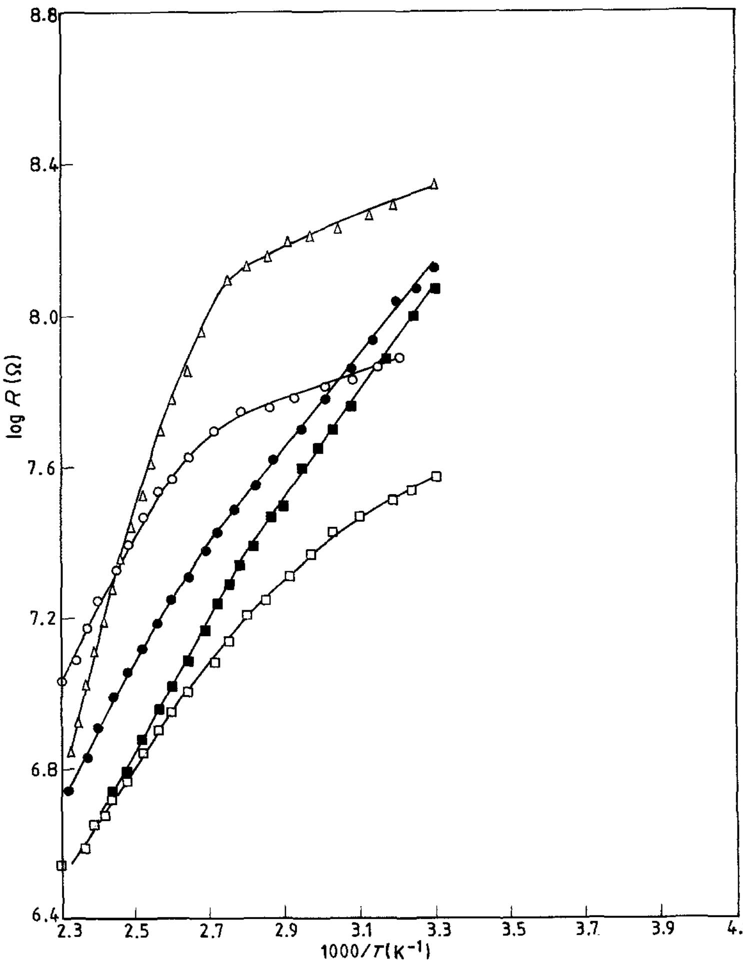

Figure 7 Plot of log R against $1/T$ for $Se_{80}Te_{20}$ films during cooling.

films have a diffuse transition (or broad transition temperature). No additional conclusions can be arrived at without ambiguity, as the transition temperature does not appear to depend systematically on the initial resistance (thickness) of the films.

Even though the plots of Fig. 4 show that during cooling, the film resistances do not reach the original values, the log R–$1/T$ plots during cooling, shown in Fig. 7, indicate that even in the low-temperature region they are linear but with a much more reduced slope than in the high-temperature region. This observation leads to the hypothesis of a possible transition back to the amorphous state while cooling beyond about 340 K. However, this hypothesis is incorrect, as the electron diffraction pattern of the heat-treated film (Fig. 5a) at room temperature shows that the film is polycrystalline. Thus, at low temperatures too, after the first heating, the films remain polycrystalline and do not undergo a reverse crystalline–amorphous transition. However, two different slopes in the high- and low-temperature regions of all the annealed films show that some transition does occur in the same temperature regions of 340 and 360 K while cooling, but to a second polycrystalline phase, rather than to the amorphous phase.

4. Conclusions

It can be concluded that the $Se_{80}Te_{20}$ films grown by vacuum deposition of bulk $Se_{80}Te_{20}$ polycrystalline alloy on to glass substrates at room temperature are amorphous in nature. Upon heating, they undergo an irreversible amorphous–crystalline transition in the temperature range 340 to 360 K. The high-resistance (thinner) films show a sharper transition than the low-resistance (thicker) films, but there is no thickness dependence of the transition temperature. Also, while cooling back, they appear to make a transition in the same temperature range, not to an amorphous phase but to a crystalline one. Thus, it appears that vacuum-deposited $Se_{80}Te_{20}$ films have a partial memory and can be brought back to, if not the same, a slightly lower electrical resistance state. However, much work is needed to state this unambiguously.

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