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Citation: *J. Appl. Phys.* **62**, 2376 (1987); doi: 10.1063/1.339502

View online: <http://dx.doi.org/10.1063/1.339502>

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# *In situ* electrical conductivity and amorphous-crystalline transition in vacuum-deposited amorphous thin films of a Se<sub>50</sub>Te<sub>50</sub> alloy

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(Received 10 March 1987; accepted for publication 7 May 1987)

*In situ* electrical conductivity measurements have been made on vacuum-deposited amorphous thin films of various thicknesses of a Se<sub>50</sub>Te<sub>50</sub> alloy in the temperature range 300–430 K. From the electrical conductivity, x-ray studies, and electron diffraction studies it is found that the as-grown films are amorphous and undergo an irreversible amorphous-crystalline transition on heating *in situ*. The amorphous-crystalline transition takes place in the temperature range 320–360 K for the different films. However, no systematic variation of the transition temperature with the thickness of the films is observed. All the films except the thinnest ones have a sharp transition temperature. X-ray and electron diffraction analyses show that the Se<sub>50</sub>Te<sub>50</sub> films above 360 K are polycrystalline. Above 360 K the electrical conductivity of the polycrystalline Se<sub>50</sub>Te<sub>50</sub> films varies as an exponential function of reciprocal temperature.

## INTRODUCTION

Many studies<sup>1–5</sup> have been made on the structure and physical properties of the bulk alloys of the Se-Te alloy system, but little is known about their behavior in the thin-film form. We have been interested in the study of the Se-Te alloy system to know more about the structure and crystallization of vacuum-deposited thin films of the system. Noda, Chow, and Kao<sup>6</sup> have observed that films of the Se<sub>1-x</sub>Te<sub>x</sub> alloy, vacuum deposited from an alloy ingot onto glass substrates kept at room temperature, tend to become polycrystalline at  $x > 0.25$ . Watanabe and Kao,<sup>7</sup> from their studies on structure and properties of Se<sub>1-x</sub>Te<sub>x</sub> films, have reported that films with  $x$  smaller than 0.5 are noncrystalline and that for films with  $x$  between 0.5 and 0.6 the structure is partly noncrystalline and partly polycrystalline. Mehra *et al.*<sup>8</sup> have reported that vacuum-deposited Te<sub>0.90</sub>Se<sub>0.20</sub>, Te<sub>0.85</sub>Se<sub>0.15</sub>, and Te<sub>0.80</sub>Se<sub>0.20</sub> films are amorphous.

We had reported in an earlier paper<sup>9</sup> about the amorphous nature of the as-grown, vacuum-deposited Se<sub>80</sub>Te<sub>20</sub> films and the amorphous-crystalline transition in them. In the present paper are described *in situ* electrical conductivity measurements and electron and x-ray diffraction studies on Se<sub>50</sub>Te<sub>50</sub> alloy thin films and the amorphous-crystalline transition in them.

## EXPERIMENT

Amorphous films of Se<sub>50</sub>Te<sub>50</sub> were prepared by evaporating the bulk polycrystalline Se<sub>50</sub>Te<sub>50</sub> alloy in a vacuum of

$5 \times 10^{-5}$  Torr onto glass substrates held at room temperature. The bulk polycrystalline alloy was prepared as follows. A stoichiometric mixture (1:1) of the elements selenium and tellurium, each of purity 99.999%, was sealed in an evacuated quartz ampoule. The ampoule was heated to a temperature of 220 °C and maintained at that temperature for 3 days and at 450 °C for 1 day. While heating, the ampoule was frequently shaken to ensure thorough mixing. The molten sample was then slowly cooled to room temperature. The bulk Se<sub>50</sub>Te<sub>50</sub> alloy formation and its crystallinity were verified by Debye-Scherrer diffraction as shown in Fig. 1. The unit-cell dimensions were found to be  $c = 5.423$  Å and  $a = 4.415$  Å, which agree well with the earlier reported values.<sup>10</sup> Table I shows a comparison of the calculated  $d$  values from the Debye-Scherrer photograph with the standard  $d$  values.<sup>10</sup> It can be seen that there is a good agreement between the two sets of  $d$  values.

Thin films of Se<sub>50</sub>Te<sub>50</sub> varying in thickness between 300 and about 2000 Å were prepared on glass substrates with tin contacts at the ends held at room temperature; the electrical resistance of the as-grown films was measured *in situ* immediately after deposition in the temperature range 300–430 K during heating and cooling in a vacuum of  $5 \times 10^{-5}$  Torr. Films of different thicknesses were prepared individually in separate depositions, and in each deposition, a given quantity of the bulk alloy Se<sub>50</sub>Te<sub>50</sub> was taken in the molybdenum boat and was completely evaporated at a fast rate. This was done to minimize fractionation of the bulk alloy during evaporation, if any, and to ensure that the average composi-

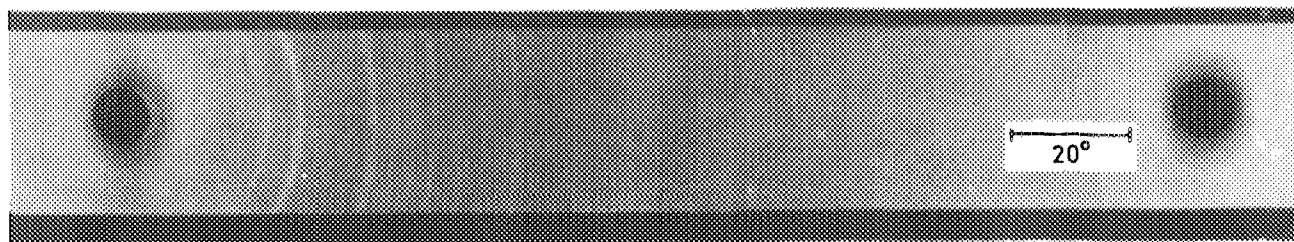


FIG. 1. X-ray powder photograph of bulk Se<sub>50</sub>Te<sub>50</sub> alloy.

TABLE I. Comparison of the calculated  $d$  values from the x-ray powder photograph with the standard  $d$  values arrived at from the previous work on the bulk  $\text{Se}_{50}\text{Te}_{50}$  alloy.<sup>10</sup>

Serial no.	$d_{\text{calc.}}$ (Å)	$d_{\text{standard}}$ (Å)	$hkl$
1	3.864	3.824	(100)
2	2.189	2.208	(110)
3	1.893	1.912	(200)
4	1.789	1.803	(201)
5	1.696	1.712	(112)
6	1.564	1.563	(202)
7	1.437	1.445	(120)
8	1.388	1.399	(113)
9	1.272	1.275	(122)

tion of the films would be nearly that of the bulk alloy.

The resistivity measurements were made only up to a temperature of about 430 K as it was found that part of the alloy film material started to evaporate above about 450 K. The thicknesses of the films were determined using a quartz crystal thickness monitor to measure their masses. The electrical resistance measurements were made using a Keithley electrometer to an accuracy of 0.01%. The temperature of the films was measured using a copper-constantan thermocouple in pressure contact with the glass substrate surface on which the film was deposited. The thermoelectromotive force was noted on a high-impedance digital panel meter to an accuracy of 0.01 mV. The films were examined both before and after heat treatment by x-ray diffraction. The films were also examined after heat treatment in the electron microscope at room temperature.

## RESULTS AND DISCUSSION

From the Debye-Scherrer diffraction photograph (Fig. 1) it is obvious that the bulk alloy formed of  $\text{Se}_{50}\text{Te}_{50}$  is

polycrystalline. Figures 2(a) and 2(b) show the x-ray diffractograms of a typical (a) as-grown and (b) annealed film. From Fig. 2(a) it is clear that the as-grown films of  $\text{Se}_{50}\text{Te}_{50}$  are amorphous as there are no observable peaks in the diffraction pattern. The observation that the as-grown thin films of the  $\text{Se}_{50}\text{Te}_{50}$  alloy are amorphous is in contrast to the observations of Noda, Chow, and Kao<sup>6</sup> and Watanabe and Kao,<sup>7</sup> who respectively find that for Te-rich alloys with Te concentration above about 25 and 50 at. %, films vacuum deposited on glass substrates at room temperature are no longer amorphous but polycrystalline. Figure 2(b) shows that the films, after heat treatment, are polycrystalline as evidenced by the (100), (101), (110), and (201) reflections. Figure 3 shows resistance versus temperature plots during heating of the films of different thicknesses between 300 and about 2000 Å. It can be seen that there is an abrupt fall of two orders in resistance of the films between 320 and 360 K. With a further increase in temperature above 360 K, the resistance decrease is very much less and hence not evident in the same plot. During cooling, the resistance increases very slowly and not sharply as in the case of heating and, as such, the cooling curves are not shown in the same plot.

It is evident from the fact that there is a sharp drop of resistance (by two orders) during heating, while there is no such sharp change of resistance during cooling, that the films undergo an irreversible transition (amorphous to crystalline) on heating and there is no reverse transition while cooling.

It is of particular interest to note from the figure that lower resistance films tend to have a broader transition and a higher transition temperature than the higher resistance films. [For example, compare the electrical resistivity versus temperature plots of films of initial resistance  $28 \times 10^8 \Omega$  (lower resistance) and  $60 \times 10^8 \Omega$  (higher resistance) in the figure.] However, it is also evident from the figure that there is no systematic variation of the amorphous-crystalline tran-

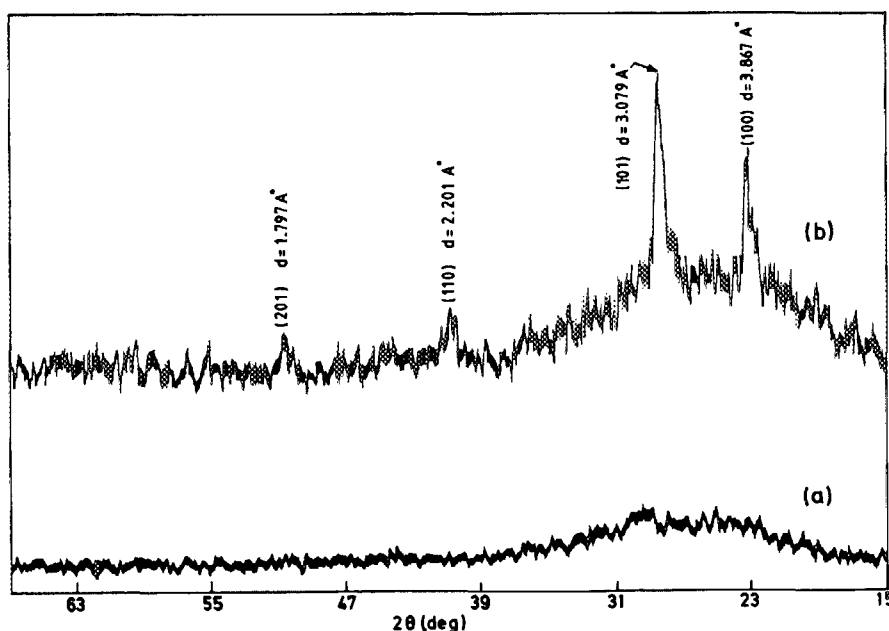


FIG. 2. X-ray diffractograms of (a) as-grown and (b) annealed  $\text{Se}_{50}\text{Te}_{50}$  films.

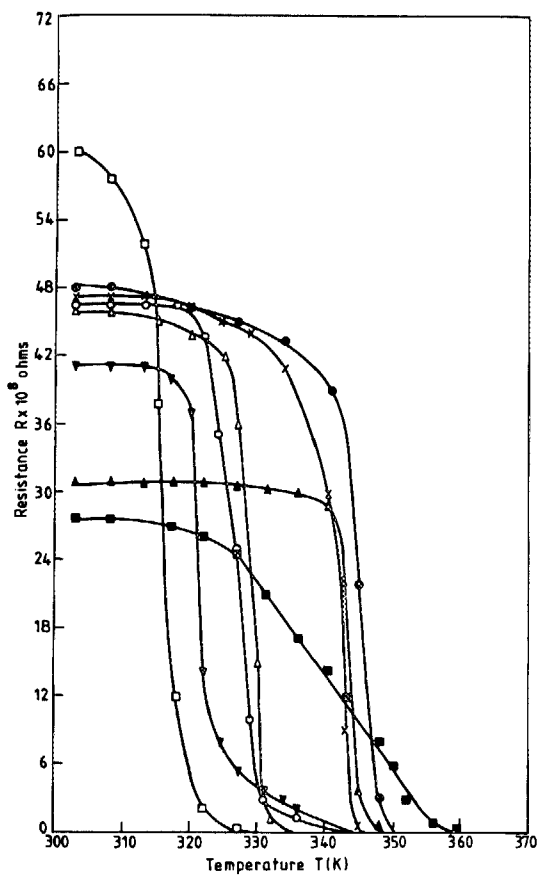


FIG. 3. Resistance against temperature plots during heating of  $\text{Se}_{50}\text{Te}_{50}$  alloy thin films (■ 310 Å, ▽ 500 Å, ○ 690 Å, × 800 Å, △ 1200 Å, □ 1550 Å, ● 1800 Å, ▲ 2000 Å).

sition temperature (the temperature of maximum slope in the  $R$ -vs- $T$  plots) with the initial resistance (thickness) of the films. Thus, it can be said that even though there is no systematic thickness dependence of the transition temperature, the low-resistance films have a higher and broader transition while the high-resistance films exhibit a lower but sharper transition.

Figures 4(a) and 4(b) show the electron diffraction pattern and micrograph of a typical heat cycled film. It is obvious from the diffraction ring pattern of Fig. 4(a) that the film is polycrystalline. The comparison of the calculated  $d$  values from the grainy ring pattern of Fig. 4(a) with those of the bulk  $\text{Se}_{50}\text{Te}_{50}$  alloy is shown in Table II. It is seen that there is a good agreement indicating that the film material is  $\text{Se}_{50}\text{Te}_{50}$ . There is also a good agreement of the  $d$  values calculated from the x-ray diffractogram of Fig. 2(b) and noted in the figure with those of the bulk  $\text{Se}_{50}\text{Te}_{50}$  alloy.

The different resistance versus temperature variations during heating and cooling for all the films and sharp irreversible fall in resistance between 320 and 360 K while heating imply that an irreversible, amorphous-to-crystalline transition takes place between 320 and 360 K during heating. The amorphous nature of the as-grown films and the polycrystallinity of the heat-treated films evidenced by the x-ray and electron diffraction patterns support the conclusion

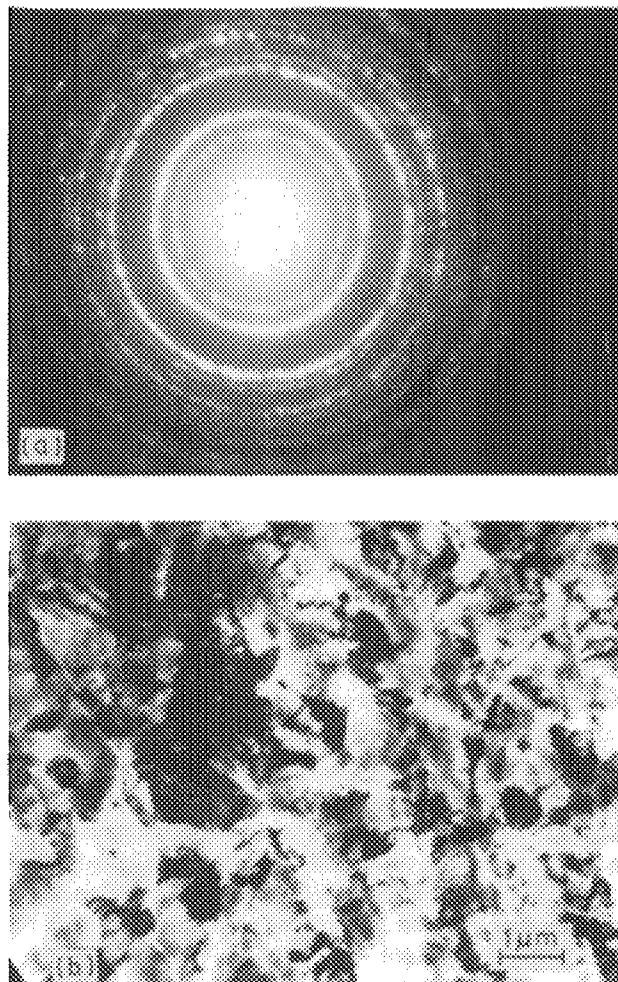


FIG. 4. (a) Electron diffraction pattern and (b) electron micrograph ( $\times 10\,000$ ) of an annealed  $\text{Se}_{50}\text{Te}_{50}$  film.

arrived at from the electrical conductivity studies that there is an irreversible amorphous-crystalline transition during heating between 320 and 360 K. The existence of a sharp irreversible fall by two orders in the electrical resistance of all the films, and the x-ray and electron diffraction evidence which show that there is an amorphous-crystalline irreversible transition during heating confirms the fact that the as-

TABLE II. Comparison of calculated  $d$  values from the electron diffraction ring pattern of Fig. 4(a) with the bulk  $d$  values of  $\text{Se}_{50}\text{Te}_{50}$ .

Serial no.	$d_{\text{calc}}$ (Å)	$d_{\text{bulk}}$ (Å)	$hkl$
1	3.637	3.824	100
2	2.643	...	...
3	2.197	2.208	110
4	1.537	1.564	202
5	1.425	1.437	120
6	1.322	1.314	203
7	1.241	1.272	122
8	1.158	1.153	302
9	1.060	1.042	303
10	0.938	0.943	205

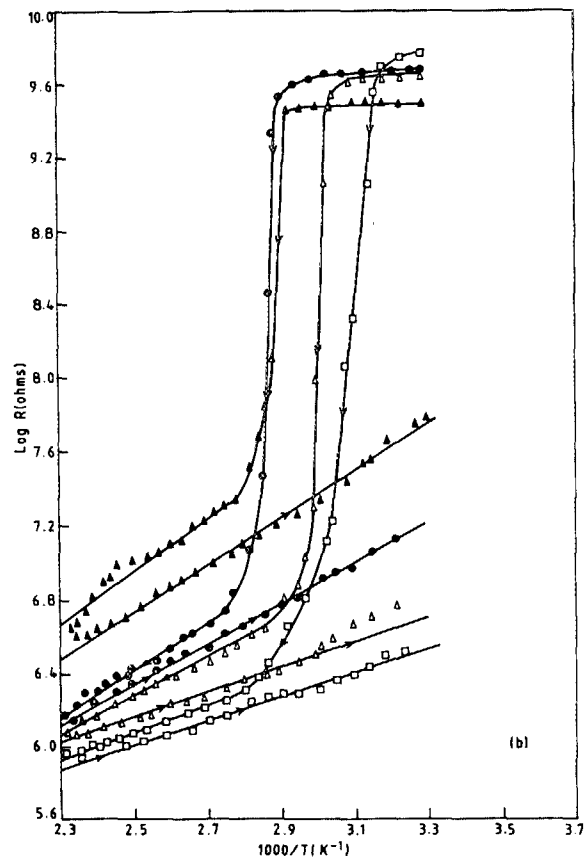
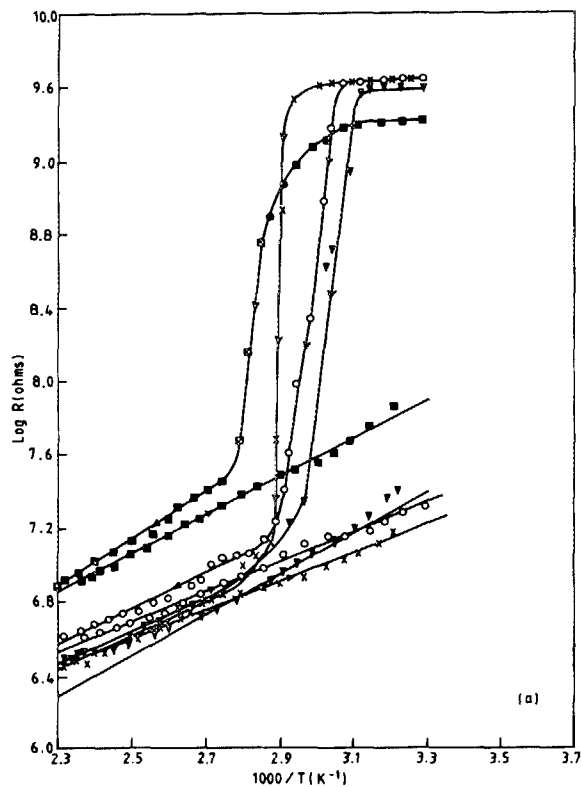


FIG. 5. Plots of  $\log R$  vs  $1/T$  for  $\text{Se}_{50}\text{Te}_{50}$  films of various thicknesses. (a) Thicknesses between 300 and 800 Å: (■) 310 Å, (▽) 500 Å, (○) 690 Å, (×) 800 Å. (b) Thicknesses between 1200 and 2000 Å (△) 1200 Å, (□) 1550 Å, (●) 1800 Å, (▲) 2000 Å.

grown thin films of  $\text{Se}_{50}\text{Te}_{50}$  alloy are amorphous.

Figures 5(a) and 5(b) are logarithmic plots of resistance versus reciprocal temperature during heating and cooling for films of different thicknesses.  $\log R$  vs  $1/T$  plots for films of thicknesses ranging from 300 to 800 Å are shown in Fig. 5(a) and between 1000 and 2000 Å in Fig. 5(b) for clarity. We find that above 360 K, during heating (i.e., after the amorphous-crystalline transition), the  $\log R$  vs  $1/T$  plots are linear for all the films of various thicknesses but their slopes are different. The activation energies calculated from their slopes vary from 0.15 to 0.26 eV. From Figs. 5(a) and 5(b) it is also apparent that below about 320 K (during the heating cycle) the  $\log R$  vs  $1/T$  plots are linear with reduced slopes showing that in the amorphous state too, possibly the film resistance behaves exponentially as  $1/T$  near and below room temperature. But nothing more specific and definite about the conductivity behavior in the amorphous state can be said as the measurements were carried out only above room temperature ( $\sim 300$  K) and hence the range of temperatures in which the films are amorphous is only 20–60 K. The  $\log R$  vs  $1/T$  plots during cooling are linear for all the films in the entire range studied (viz. 300–430 K) with the activation energy value ranging again between 0.15 and 0.26 eV as in the case of heating. It must be pointed out that this observation of linearity of the  $\log R$  vs  $1/T$  plots in the entire range during cooling (i.e., in the polycrystalline state) is in contrast to the behavior of  $\text{Se}_{80}\text{Te}_{20}$  thin films reported earlier<sup>9</sup> where the  $\log R$  vs  $1/T$  plots during cooling departed

from linearity and became sublinear at low temperatures, resulting, in some cases, in two different slopes in the high- and low-temperature regions. This led us to postulate a crystalline-crystalline phase transition in the case of  $\text{Se}_{80}\text{Te}_{20}$  thin films while cooling, at around the same temperature as during heating.

## CONCLUSIONS

On the basis of the observations made, it can be concluded that  $\text{Se}_{50}\text{Te}_{50}$  films vacuum deposited from the bulk polycrystalline alloy onto glass substrates at room temperature are amorphous in nature. This is in contrast to the observations of Noda, Chow, and Kao<sup>6</sup> and Watanabe and Kao.<sup>7</sup> From the temperature behavior of conductivity, it can be said that they undergo an irreversible transition from an amorphous to a crystalline phase between 320 and 360 K. There does not appear to be any systematic variation of the transition temperature with thickness. However, low-resistance films tend to have a broad transition and a higher transition temperature.

$\log R$  vs  $1/T$  plots of the polycrystalline  $\text{Se}_{50}\text{Te}_{50}$  thin films (during cooling) are linear in the entire temperature range studied in contrast to the behavior of  $\text{Se}_{80}\text{Te}_{20}$  films reported earlier.<sup>9</sup>

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