# ELECTRICAL TRANSPORT PROPERTIES OF COPPER-DOPED TELLURIUM FILMS

#### P. C. MATHUR

Department of Physics and Astrophysics, University of Delhi, Delhi 110007 (India)

A. L. DAWAR

Defence Science Laboratory, Metcalf House, Delhi 110054 (India)

O. P. TANEJA

Government College, Gurgaon, Haryana (India) (Received July 20, 1979; accepted July 23, 1979)

Polycrystalline films of copper-doped tellurium were grown by co-evaporating copper and tellurium from separate boats. Measurements were made of the electrical transport properties of these films. It was observed that the addition of copper decreases the activation energies of both the conductivity and the mobility. The low temperature conduction data were interpreted on the basis of a variable range hopping mechanism while the high temperature data indicate the dominance of the grain boundary scattering mechanism.

#### 1. INTRODUCTION

The structural and electrical properties of thin films of tellurium have been studied by several workers<sup>1-8</sup> owing to their wide application in the fabrication of various devices such as infrared detectors<sup>9</sup>, thin film field effect transistors<sup>10,11</sup> and strain-sensitive elements<sup>12</sup>. As tellurium is an elemental semiconductor, films of this element are free from stoichiometric defects. Evaporated tellurium films usually show p-type conduction owing to the presence of lattice defects which serve as acceptors. Dutton and Muller<sup>6</sup> and Goswami and Ojha<sup>7</sup> have observed that over a large temperature range the variation of the Hall mobility with temperature for polycrystalline tellurium films exhibits a  $\frac{3}{2}$  power dependence which indicates the predominance of ionized impurity scattering. However, Okuyama and Kumagai<sup>1</sup> and Capers and White<sup>8</sup> have obtained evidence for the dominant role of the grain boundary scattering mechanism in tellurium films in agreement with Petritz model<sup>13</sup>:

$$\mu_{\rm H} = \mu_0 \exp(-W_1/kT) \tag{1}$$

where  $\mu_0$  is a constant which depends on the evaporation parameters and  $W_1$  is the mobility activation energy. Phahle<sup>2</sup> and Goswami and Ojha<sup>7</sup> have observed two characteristic activation energies, 0.01 eV and 0.18 eV, which correspond to low and high temperature regions respectively.

In the present paper we report experimental results on the effect of copper doping in tellurium films on the temperature variation of the Hall coefficient  $R_{\rm H}$ , the d.c. conductivity  $\sigma$  and the Hall mobility  $\mu_{\rm H}$ . It was observed that the conductivity and the mobility increase with an increase in the copper concentration whereas the Hall coefficient  $R_{\rm H}$  and the mobility activation energy decrease. The mechanism of

the low temperature conduction was interpreted as variable range hopping while the high temperature data indicate the dominance of the grain boundary scattering mechanism.

### 2. EXPERIMENTAL DETAILS

Rectangular films of size 35 mm × 6 mm were grown on ultrasonically cleaned glass substrates which were maintained at room temperature by evaporating tellurium under a high vacuum ( $5 \times 10^{-6}$  Torr). Copper-doped films were fabricated by co-evaporating copper and tellurium from two separate boats. The rate of evaporation of the tellurium was 25 Å s<sup>-1</sup> for all the films and was controlled by a quartz crystal thickness monitor<sup>14</sup>. Careful control was exercised over the evaporation rate of the copper in order to obtain films of the required compositions. The concentrations of copper doped into the films, shown in Table I, were calculated on the basis of the evaporation rates of the constituents. The sticking coefficients of the materials on quartz and glass were assumed to be the same for the purpose of calculating the dopant concentration. All the films were grown to a thickness of 3500 Å. Electron micrographs revealed that the structure of the films was polycrystalline and that the size of the microcrystallites ranged from 200 to 1200 Å. High purity gold was evaporated onto the films under a high vacuum to provide electrical contacts. The current contacts were spread over the entire width of the films while the voltage contacts were only dots of approximate diameter 0.5 mm. The five-probe technique, as described by Putley<sup>15</sup>, was used to measure the Hall coefficient and d.c. conductivity. The ohmic nature of the contacts was verified throughout the temperature range by the linearity of the I-V characteristics. The directions of the current and the magnetic field B (about 5 kG) were reversed to eliminate any error due to the thermomagnetic effects. The influence of the geometry of the films on the Hall measurements was neglected as the length-to-width ratio was greater than 4. The variation of the Hall coefficient with temperature was found to be reproducible over two or three runs, indicating that the structure of the films was fixed by annealing. The Hall coefficient was found to be independent of the magnetic field and sample current. The overall error in the Hall mobility  $(R_H\sigma)$  was estimated to be about 5%. A copper block was used to mount the sample which was also kept in a Dewar flask containing liquid nitrogen. A copper-constantan thermocouple, which was soldered to the copper block, was used to measure the temperature.

TABLE I

Film	Conductivity activation energy $W_2$ (eV)	Mobility activation energy $W_1$ (eV)	Peak temperature T <sub>m</sub> (K)	T <sub>0</sub> (K)	N(E) (eV <sup>-1</sup> cm <sup>-3</sup> )
Undoped tellurium	0.41	0.20	192	1780	$1.05 \times 10^{23}$
Copper-doped tellurium (0.8%)	0.29	0.14	213	915	$2.04\times10^{23}$
Copper-doped tellurium (1.4%)	0.19	0.10	220	410	$4.6\times10^{23}$

## 3. RESULTS AND DISCUSSION

The observed variation of  $R_{\rm H}$  with temperature (log  $R_{\rm H}$  versus 1/T) for all the films is shown in Fig. 1. The value of  $R_{\rm H}$  is observed to increase with temperature in the low temperature region, to attain a maximum at a temperature  $T_{\rm m}$  and then to decrease as the temperature is further increased. A similar variation of  $R_{\rm H}$  with temperature has been reported for single-crystal tellurium by Shalyt and Obratzsov<sup>16</sup> and Fukuroi et al.<sup>17</sup> The increase in  $R_{\rm H}$  with temperature in the low temperature region can be explained<sup>18</sup> in terms of two impurity levels  $E_1$  and  $E_2$ . The level  $E_1$  lies within the valence band below the edge  $E_0$  whereas the level  $E_2$  is deep and is situated within the band gap. The level  $E_1$  acts as a trap which reduces the carrier concentration and thereby increases  $R_{\rm H}$  as the temperature is increased. The level  $E_2$  becomes activated at  $T_{\rm m}$ , corresponding to the peak in Fig. 1. This activation increases the carrier concentration and decreases  $R_{\rm H}$  as the temperature is further increased.

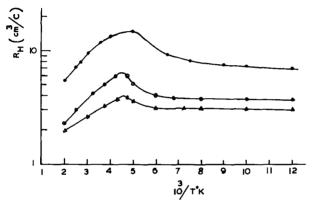


Fig. 1. Variation of the Hall coefficient with temperature: —●—, undoped tellurium films; —○—, copper-doped (0.8%) tellurium films; —△—, copper-doped (1.4%) tellurium films.

The value of  $R_{\rm H}$  is found to decrease with an increase in the copper concentration in the films. This effect is due to the copper becoming substituted at tellurium vacancies, thus increasing the concentration of acceptors<sup>19</sup>. It is also observed from Fig. 1 that as the concentration of copper increases the value of  $T_{\rm m}$  also increases. This effect can be understood from the fact that, as the charge carrier concentration increases with the increase in copper concentration in the film, the shallow impurity energy level  $E_1$  shifts towards the valence band edge and the number of carriers that are trapped by this impurity level is thus decreased. The onset of the activation of the deep impurity level  $E_2$  will therefore occur at a higher temperature in samples with a higher charge carrier concentration. This explanation is consistent with the observed decrease of the slope of  $\log R_{\rm H}$  versus 1/T in the low temperature region.

The variation of conductivity with temperature ( $\log \sigma$  versus 1/T) for all the films is shown in Fig. 2(a). It is observed that for all the films the conductivity in the

high temperature region obeys the relation

$$\sigma \propto \exp(-W_2/kT) \tag{2}$$

where  $W_2$  is the conductivity activation energy, values of which are shown in Table I. It is observed that the value of  $W_2$  decreases with an increase in the copper concentration. This shows that the grain boundary barrier potential decreases with an increase in the copper concentration. The low temperature data (Fig. 2(b)) for all the films are consistent with the relation

$$\sigma \propto \exp\{(-T_0/T)^{1/4}\}\tag{3}$$

This behaviour indicates the occurrence of the variable range hopping conduction mechanism. The existence of the localized states necessary for such a conduction process is a consequence of imperfections associated with polycrystalline tellurium films. The values of  $T_0$  for all the films, which are shown in Table I, are related to the density N(E) of localized states by

$$N(E) = \frac{16\alpha^3}{kT_0} \tag{4}$$

where  $\alpha = 10^7$  cm<sup>-1 20</sup>. The values of N(E) are also shown in Table I.

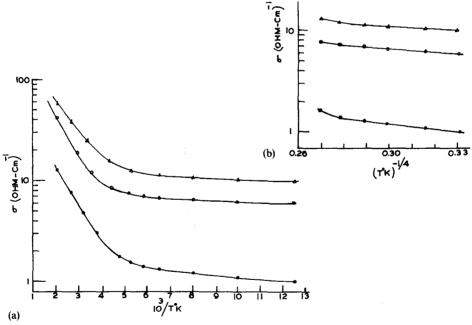


Fig. 2. Variation of the conductivity with temperature:  $-\bullet$ —, undoped tellurium films;  $-\bigcirc$ —, copperdoped (0.8%) tellurium films;  $-\bigcirc$ —, copper-doped (1.4%) tellurium films.

The variation of the Hall mobility with temperature ( $\mu_H$  versus 1/T) for all the films is shown in Fig. 3 and is found to follow the Petritz relation:

$$\mu_{\rm H} = \mu_0 \exp(-W_1/kT) \tag{5}$$

where  $\mu_0$  is a constant which depends on the evaporation parameters. It is observed from this figure that for all the films the low temperature activation energy is very much smaller than that at high temperatures, as shown in Table I. For a given film the mobility activation energy in the high temperature region is about one-half of the conductivity activation energy. This shows that in the high temperature region the conduction mechanism does not involve localized states and is a free charge carrier process dominated by scattering at grain boundary potential barriers.

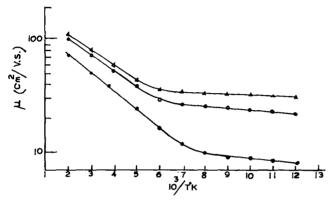


Fig. 3. Variation of the Hall mobility with temperature:  $-\bullet$ —, undoped tellurium films;  $-\bigcirc$ —, copper-doped (0.8%) tellurium films;  $-\triangle$ —, copper-doped (1.4%) tellurium films.

#### REFERENCES

- 1 K. Okuyama and Y. Kumagai, Jpn. J. Appl. Phys., 12 (1973) 1884.
- 2 A. M. Phahle, Thin Solid Films, 41 (1977) 235.
- 3 A. Kubovy and M. Janda, Phys. Status Solidi A, 36 (1976) 101.
- 4 A. Kubovy and M. Janda, Phys. Status Solidi A, 35 (1976) 471.
- 5 M. Janda and A. Kubovy, Phys. Status Solidi A, 35 (1976) 391.
- 6 R. W. Dutton and R. S. Muller, Proc. IEEE, 59 (1971) 1511.
- 7 A. Goswami and S. M. Ojha, Thin Solid Films, 16 (1973) 187.
- 8 M. J. Capers and M. White, Thin Solid Films, 15 (1973) 5.
- 9 J. Crosvalet and C. Jund, IEEE Trans. Electron Devices, 14 (1967) 777.
- 10 H. L. Wilson and W. A. Gutierretz, Proc. IEEE, 55 (1967) 415.
- 11 Y. Yasuoka, H. Hirayama and T. O. Miyata, Jpn. J. Appl. Phys., 16 (1977) 1195.
- 12 J. Conragan and R. S. Muller, Solid State Sensors Symp., Seattle, Wash., 1970, IEEE Catalog Number 70C25-SENSOR, 1970, p. 52.
- 13 R. L. Petritz, Phys. Rev., 104 (1956) 1508.
- 14 J. Izeng Lue, J. Phys. E, 10 (1976) 161.
- 15 E. H. Putley, The Hall Coefficient and Related Phenomena, Butterworth, London, 1960, p. 42.
- 16 S. S. Shalyt and Y. U. Obratzsov, Zh. Tekh. Fiz., 27 (1957) 189.
- 17 T. Fukuroi, S. Tanuma and S. Tobisawa, Sci. Rep. Res. Inst. Tohoku Univ. Ser. A, 4 (1952) 283.
- 18 E. Klotynsh, Phys. Status Solidi, 21 (1974) 377.
- 19 H. Kronmuller, J. Taumann and K. Seiler, Z. Naturforsch., Teil A, 11 (256) 243.
- 20 J. Tauc, Amorphous and Liquid Semiconductors, Plenum, London, 1974.