Electrical properties of mercury telluride

1964 Br. J. Appl. Phys. 15 151

(http://iopscience.iop.org/0508-3443/15/2/305)

BRIT. J. APPL. PHYS., 1964, VOL. 15

Electrical properties of mercury telluride

W. GIRIAT†

Department of Applied Physics, University of Durham

MS. received 7th August 1963, *in revised form 7th October* 1963

Abstract. Electrical conductivity, Hall coefficient, magnetoresistance and thermoelectric power have been measured for HgTe single crystals, both undoped and doped with Pb from 2×10^{17} cm^{-3} up to 6×10^{20} cm^{-3}, in the temperature range 77–400° K. The properties of HgTe are independent of the concentration of Pb and strongly dependent on the annealing process. The Hall coefficient at low temperatures changes considerably in magnetic fields greater than 900 Oe. The Hall mobility at 77° K is above 70 000 cm^2 v^{-1} sec^{-1}. The HgTe–PbTe system, prepared by the method used here, is two phase.

1. Introduction

By reason of the very small energy gap and small effective mass, HgTe is one of the interesting semiconductors whose properties are in the transition region between semiconductors and metals. The first work on HgTe (Nikol'skaya and Regel 1955) was carried out on pressed samples which have an electron mobility of about 12 000 cm^2 v^{-1} sec^{-1}. Several authors investigated the properties of HgTe (Carlson 1958, Harman *et al.* 1958, Black *et al.* 1958, Lawson *et al.* 1959, Strauss *et al.* 1962). Real progress in this field was made by the discovery (Rodot and Triboulet 1962, Quilliet 1962, Quilliet *et al.* 1962) that annealing of HgTe in the presence of mercury vapour improved the properties of this material and it became possible to obtain intrinsic material with an electron mobility above 30 000 cm^2 v^{-1} sec^{-1}.

The object of this work was to determine the properties of the HgTe–PbTe system and the properties of single crystals of HgTe, both undoped and doped with Pb.

2. The HgTe–PbTe system

The preparation of the HgTe–PbTe system has been attempted. Two methods were used. In the first method finely powdered HgTe and PbTe were mixed together in appropriate quantities. The mixture was put in a silica tube and sealed off *in vacuo* and heated for 300 hours at a temperature 20 degc below the estimated melting point and then cooled slowly (10 degc h^{-1}) to room temperature. It was assumed for this estimation that the melting point changes linearly with composition ($t_{\mathrm{mp}} = 670°$ c for HgTe and $t_{\mathrm{mp}} = 904°$ c for PbTe). Compositions were prepared with 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 95% PbTe in HgTe. In the second method all these compositions were prepared by directly melting together in silica tubes *in vacuo* appropriate quantities of HgTe and PbTe. They were heated for 36 hours at a temperature 150 degc above the melting point and slowly cooled (4 degc h^{-1}) to room temperature. X-ray photographs and metallurgical analyses show that the whole of this system (from 5 to 95% PbTe in HgTe) is two phase with both the above methods of preparation. The phases appeared to be HgTe and PbTe.

3. Preparation of single crystals of HgTe, both undoped and doped with Pb

For preparation of the HgTe, the mercury and the tellurium were both distilled several times *in vacuo* and the Te was then zone refined (30 zone) (Giriat and Dziuba 1959). Stoichiometric quantities of the Hg and Te were placed in a silica tube A connected to a second silica tube B which could be water cooled. Both tubes had previously been thoroughly

---

† On leave from the Institute of Physics, Polish Academy of Science, Warsaw (present address).

outgassed. In the first stage of preparation material was distilled *in vacuo* from the tube A to the water cooled tube B. This process removed gas which was occluded on the Hg, the Te and on the silica tubes. When all the material was distilled to the cool tube B, the tubes A and B together were sealed off. The material was then redistilled from tube B to tube A and A was sealed off. After this process the material was ready to be reacted, still in the tube A. This method was invented for HgTe by Dziuba (1964). The reaction was carried out at 500°c for 15 hours and then the temperature was increased to 750°c and slowly lowered. Single crystals were prepared by the Bridgman method, again in the same tube A, without unsealing. When preparing single crystals of doped HgTe appropriate quantities of Pb were introduced into the silica tube before the reaction. The rest of the treatment was the same. Undoped single crystals of HgTe and crystals doped by adding Pb of concentration 2×10^{17} cm^{-3}, 2×10^{18} cm^{-3}, 2×10^{19} cm^{-3}, 2×10^{20} cm^{-3} and 6×10^{20} cm^{-3} were prepared. The results of the spectral analysis indicated the presence of the same quantity of Pb as had been introduced.

4. Preparation of samples and measurement

Rectangular samples for electrical measurement were cut from single crystals of HgTe, both undoped and doped with Pb as above. The size of the samples was 1·5 mm × 2·5 mm × 12·0 mm. Measurement of Hall coefficient R_H and electrical conductivity σ were made by using the standard d.c. method. Measurement was carried out for samples as prepared and after periods of annealing, up to 300 hours in all, in mercury vapour at either 250 or 300° c. R_H and σ were measured at intervals with several hours of annealing in between. Measurement was made in the temperature range from 77–400° K. In contrast to reported results (Rodot and Triboulet 1962, Quilliet *et al.* 1962) it was found that below room temperature the Hall coefficient for annealed samples of HgTe is dependent on the strength of the magnetic field. For this reason measurement of R_H was carried out at a field of 460 Oe.

5. Experimental results

The measurement was carried out for undoped samples and samples doped with Pb (concentration of Pb as stated above). The electrical properties of HgTe were found to be independent of concentration of Pb. The properties for unannealed materials changed from sample to sample and it seems that these changes were due to differences in the cooling process. In figures 1 and 2, σ and R_H are shown for samples which at 77° K have a positive R_H (denoted as samples A) and for samples which at 77° K have negative R_H (denoted as

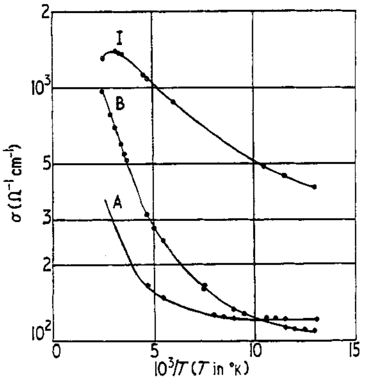

Figure 1. Temperature dependence of electrical conductivity for HgTe samples before (curves A and B) and after (curve I) annealing.

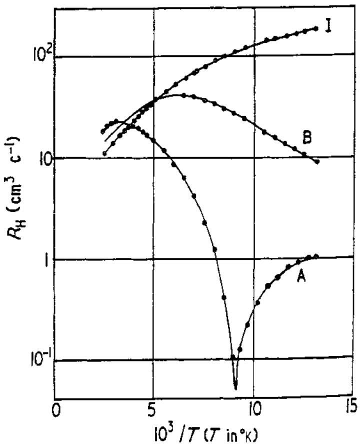

Figure 2. Temperature dependence of Hall coefficient for HgTe samples before (curves A and B) and after (curve I) annealing.

samples B). The thermoelectric power α for these samples are shown in figure 7. Values of R_H, σ and α for all other samples were between those for A and B. All these samples were annealed in mercury vapour at temperatures of either 250° C or 300° C. All samples had the same behaviour after annealing, whether A or B or intermediate. It was found, in agreement with previous reports, that the Hall coefficient, as well as the electrical conductivity, was increased by annealing and that all the samples became n-type. The product $R_H\sigma$ increased by over two orders of magnitude at 77° K.

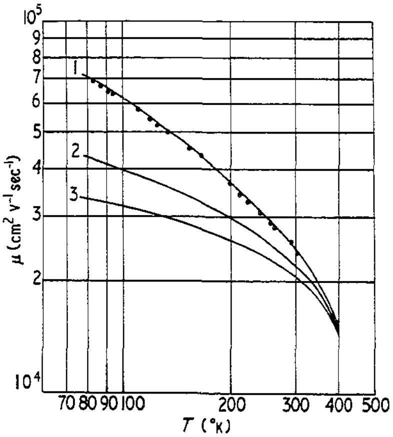

Figure 3. Temperature dependence of electron Hall mobility for HgTe samples after annealing.

The Hall coefficient and electrical conductivity have maximum values after about 100 hours annealing at 250° C (and a somewhat shorter time for annealing at 300° C). If the annealing process is continued the Hall coefficient and electrical conductivity begin to decrease. After 200 hours annealing the values of R_H and σ are about 80% of the maximum. Annealing for more than 200 hours caused further decrease of R_H and σ.

Samples doped with Pb more quickly reached the maximal value of R_H and σ. For the same conditions of annealing, samples doped with 6×10^{20} cm^{-3} Pb reached the maximal value of R_H and σ after about 20 hours of annealing. Annealed to the maximum value of R_H and σ, all the samples investigated have the same properties independent of the concentration of Pb.

Figure 1 shows the temperature dependence of approximately the maximum electrical conductivity for annealed samples (curve 1) and figure 2 shows the Hall coefficient (curve 1.) Figure 3 shows the temperature dependence of the Hall mobility of electrons for the optimum annealing time (curve 1), and for samples heated beyond the optimum time (curves 2

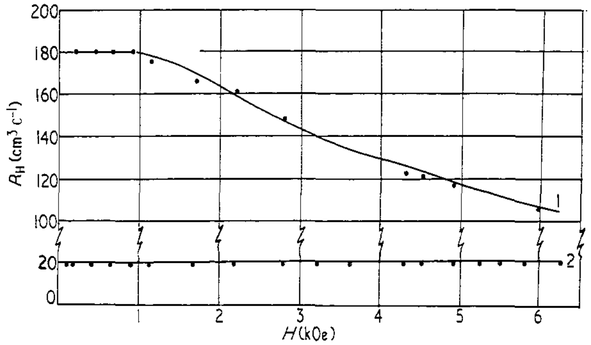

Figure 4. The Hall coefficient of annealed HgTe samples plotted against magnetic field. Curve 1, for 77° K; curve 2, for 294° K.

and 3). Curve 2 is for annealing period of 100 hours and curve 3 for 200 hours beyond the optimum annealing time. For all annealed samples the Hall coefficient showed dependence on the magnetic field below room temperature. Figure 4 shows the Hall coefficient as a function of magnetic field, and figure 5, the variation with temperature of the dependence of the Hall coefficient on magnetic field. Figure 6 shows the transverse magnetoresistance effects in annealed samples of HgTe. This figure also gives the geometry of the samples used for measurement of magnetoresistance. Results of the preliminary measurement of thermoelectric power α are shown in figure 7. All the samples before annealing have positive α at 77° K. After annealing for all samples α is negative and in a wide temperature range has a constant value.

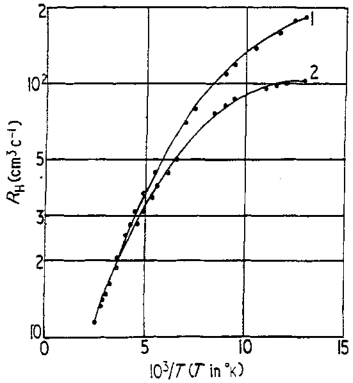

Figure 5. Temperature dependence of Hall coefficient in magnetic field. Curve 1, for 460 Oe; curve 2, for 6250 Oe.

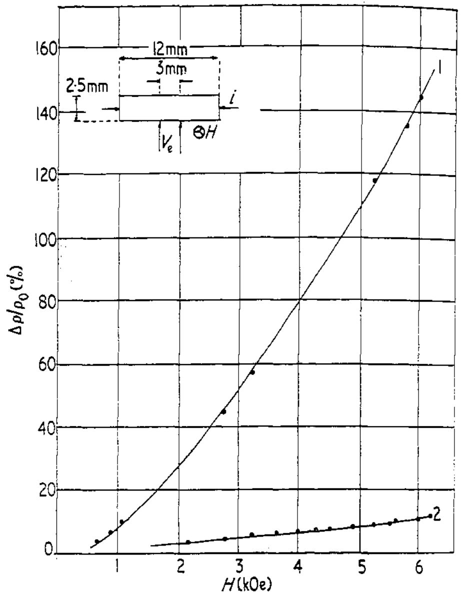

Figure 6. The transverse magnetoresistance for annealed samples HgTe for temperature 77° K (curve 1) and 294° K (curve 2).

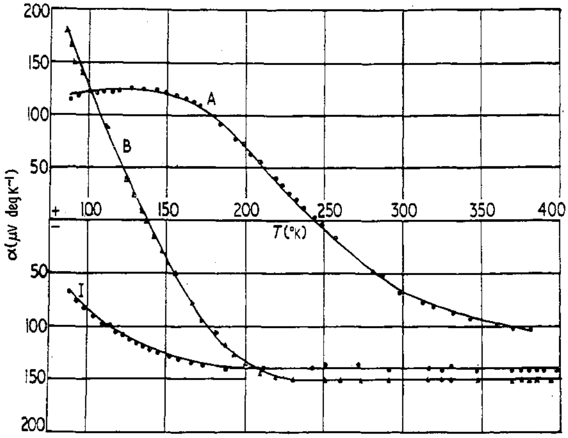

Figure 7. Thermoelectric power as a function of temperature for HgTe samples before annealing (curves A and B) and after annealing (curve I).

6. Discussion

The electrical properties of HgTe are independent of concentration of Pb up to 6×10^{20} cm^{-3}. It is a well-known experimental fact that HgTe always has an excess of Te. A little free Hg always remains present in the tube in the preparation of HgTe. In a recent published paper (Delves and Lewis 1963) the phase diagram for the system Hg–Te is given at the composition HgTe. When prepared in the normal way, HgTe has about 1% excess of Te. It is possible to reduce the free Hg considerably by completely outgassing the material before the reaction (Gałązka 1964).

In the annealing process two reactions take place. In the first reaction microheterogeneous precipitates that were contained in the non-annealed samples are dissolved (Quilliet *et al.* 1962). In the second reaction Hg atoms go into the HgTe from the Hg vapour. This process ultimately makes the HgTe compounds stoichiometric. A third effect may occur, i.e. an increase in the uniformity of the concentration of excess tellurium, so long as it remains present.

These reactions lead to the observed increase in electron concentration and therefore in σ, R_H and $R_H\sigma$. If the annealing process is continued after the stoichiometric composition is reached, HgTe begins to have an excess of Hg. This explains the reduction of the Hall coefficient for samples annealed beyond the optimum annealing time. The reduction in σ as a result of continued annealing must be due to an increase in scattering associated with the introduction of the Hg. This view is supported by the plots of $R_H\sigma$ against T in figure 3.

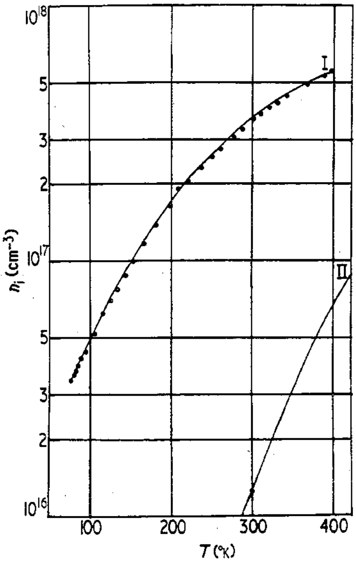

Figure 8. Temperature dependence of intrinsic carrier concentration in HgTe (curve I) and InSb (curve II).

It seems that atoms of Pb introduced into the HgTe occupy the vacancies resulting from the stoichiometric deficiency of mercury. If so, it is easy to understand why heavily doped HgTe has a short annealing time for reaching the maximal value of R_H and σ. In this case the first reaction is the most important and only a comparatively small quantity of Hg from the vapour is introduced.

HgTe, after annealing to the maximum value, is intrinsic since log $(R_H T^{3/2})$ is linear with $1/T$. Intrinsic carrier concentrations (calculated from $n_i = 1/eR_H$)† are shown in figure 8 (curve I). On this figure are also given, for comparison, the intrinsic carrier

---

† It can be seen from figures 1 and 2 that the mobility ratio μ_e/μ_h is above 500 at temperatures near 77° K.

concentration for InSb (curve II). The Hall mobility of electrons increases with decrease of temperature and by 77° K attains a value above 70 000 cm^2 v^{-1} sec^{-1} and does not show any sign of saturating. The mobility satisfies the relation $\mu \sim T^{-n}$, where $n = 2 \cdot 1$ for the temperature range 330–400° K and $n = 0 \cdot 65$ near 77° K. This indicates that in HgTe in the upper range of temperature acoustic mode lattice scattering predominates, but for temperatures near 77° K the influence of impurity scattering increases (n decreases). Electrical conductivity in the temperature range from 77 to 330° K increases with increase of temperature because the increase in n_i outweighs the decrease in mobility. For temperatures above 330° K the electrical conductivity begins to fall as temperature rises owing to the steeper decrease in mobility.

Magnetoresistance satisfied the relation $\Delta\rho/\rho_0 = H^n$, where n is between $1 \cdot 5$ and $1 \cdot 0$. The variation of the Hall coefficient with the magnetic field may be due either to the presence of two types of carrier, or to a complicated energy band structure.

From the normal band theory approximation for electron concentration

$$n = \frac{2(2\pi m^* kT)^{3/2}}{h^3} \exp \frac{\eta}{kT}$$

where η refers to the position of the Fermi level. Since the mobility ratio is very high and since acoustic lattice scattering occurs, the formula for α has the form

$$\alpha = \pm \frac{k}{e}\left(2 - \frac{\eta}{kT}\right).$$

Using these simple formulae, the value for the effective mass of electrons for annealed samples is $m^* = 0 \cdot 035\ m_0$, which is constant in the temperature range from 215–400° K. The assumptions of these formulae, i.e. non-degenerate electron gas and spherical energy surfaces are, however, not strictly fulfilled here. Nevertheless, the error will not be large since η is nearly zero.

Acknowledgments

I wish to express my appreciation to Professor D. A. Wright for suggesting the problem and for his encouragement and valuable discussions. I wish to thank S. F. Reddaway and P. M. Spencer for their kind help in the preparation of this paper. I am indebted to the Polish Academy of Science and to the Atomic Energy Research Establishment, Harwell for a grant.

References

Black, J., Ku, S. M., and Minden, H. T., 1958, *J. Electrochem. Soc.*, **105**, 723.
Carlson, R. O., 1958, *Phys. Rev.*, **111**, 476.
Delves, R. T., and Lewis, B., 1963, *J. Phys. Chem. Solids*, **24**, 549.
Dziuba, Z., 1964, *Acta Phys. Polon.*, in the press.
Gatązka, R., 1964, *Acta Phys. Polon.*, in the press.
Giriat, W., and Dziuba, Z., 1959, *Acta Phys. Polon.*, **18**, 589.
Harman, T. C., Logan, M. J., and Goering, H. L., 1958, *J. Phys. Chem. Solids*, **7**, 228.
Lawson, W. O., Nielsen, S., Putley, E. H., and Young, A. S., 1959, *J. Phys. Chem. Solids*, **9**, 325.
Nikol'skaya, E. I., and Regel, A. R., 1955, *Zh. Tekh. Fiz.*, **25**, 1352.
Quilliet, A., 1962, *J. Phys. Radium*, **23**, 93.
Quilliet, A., Rodot, H., and Rodot, M., 1962, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (London: The Institute of Physics and The Physical Society), p. 711.
Rodot, H., and Triboulet, R., 1962, *C. R. Acad. Sci., Paris*, **254**, 852.
Strauss, A. J., Harman, T. C., Mavroides, J. G., Dickey, D. H., and Dresselhaus, M. S., 1962, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (London: The Institute of Physics and The Physical Society), p. 703.