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On the Preparation and Electrical Properties of $PtSb_2$

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The preparation and the Czochralski growth of single crystals of $PtSb_2$ by a liquid encapsulation technique is described. Conductivity and Hall effect measurements have been made in the temperature range 20 to 300° K. It is found that the material is n-type, with a carrier concentration of about $6 \times 10^{16}/cm^3$, the ratio of electron to hole mobility, μ_e/μ_h, is 0.57 at 110° K, and the electron mobility has a maximum value of 2100 cm^2/V sec at 50° K. The thermal energy gap is 0.112 eV.

1. Introduction

Various reports have appeared concerning the growth and properties of single-crystal $PtSb_2$ [1-3]. $PtSb_2$ has the pyrite (C2 type) structure [4], melts congruently at 1226° C [5], and is a semiconductor with a reported energy gap $E°_g \simeq 0.075$ eV [2].

In describing the preparation and Czochralski growth (pulling) of $PtSb_2$, Miller *et al* [1] report that weight losses, assumed to be of antimony, of up to 0.5% were observed in initial melts. Additional antimony was added and the material remelted, and this process was repeated until the total weight reached "a nearly stoichiometric value". Crystals were pulled under N_2 from a graphite crucible at 4 cm/h with a rotation rate of 5 rev/min.

We wish to report the growth of $PtSb_2$ crystals, using a liquid encapsulation technique, and the electrical properties of these crystals. The liquid encapsulation technique for the prevention of material loss from volatile melts and also for the protection of melts in crystal pulling is now well known, and has found wide use in the growth of GaAs and other materials having volatile constituents [6-9]. The technique, as its name implies, involves the covering of a melt by a layer of an inert liquid, in this case B_2O_3, such that an ambient pressure in excess of the pressure exerted by the volatile constituents of the melt can prevent the loss of vapour from the melt surface. In the case of B_2O_3 one has the additional advantage that the encapsulant is a good solvent for most oxides, and thus the melt surface is kept clean.

2. Experimental

Platinum was supplied by Johnson Matthey and Co Ltd* and was especially selected, for its low impurity content, from the ½ in. (1.0 in. = 2.5 cm) square bars from which the highest grade thermocouple wire is made. No exact impurity content was given. Antimony was zone refined material of ultra high purity. B_2O_3 was supplied by British Drug Houses Ltd† and was of the highly pure and especially dried grade developed for liquid encapsulation. The B_2O_3 was additionally baked out at ~1000° C in a Pt crucible under vacuum to remove final traces of water and to form the B_2O_3 into ~25 g caps which fitted closely into the silica crucibles used.

The silica crucibles were placed in a close fitting graphite susceptor which was supported within the silica envelope of a standard RRE type crystal puller. The initial seed was a polycrystalline $PtSb_2$ ingot cast in a quartz tube for the purpose. An atmosphere of 1.1 to 1.5 atm of high purity N_2 was maintained in the system throughout. The susceptor was heated by RF induction.

Stoichiometric quantities of Pt and Sb were weighed into the crucible, the B_2O_3 cap placed

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on top, and the whole placed in the puller. Three or more flushes of N_2 were given before heating. Reaction took place with a considerable evolution of heat when the temperature reached 700 to 800° C. The B_2O_3 was by this time quite fluid and no loss of material was observed at this stage. The reaction product was in the form of a porous mass, and on one occasion a peak of $PtSb_2$ projecting above the B_2O_3 level gave rise to a very slight loss of material on further heating. In all other cases the product was entirely encapsulated and no loss was observed while the material was heated to its melting point. Clean bright melts were obtained.

Single crystals were obtained by seeding on to the polycrystalline seed, and pulling a neck of 1 to 3 mm diameter and 8 to 10 mm length before growing out to form the crystal. Crystals grew with a bright surface with the result that the B_2O_3 did not always coat the surface of the crystal as it emerged from the surface of the encapsulant, and there were sometimes signs of slight vapour etching on the crystal surface. There was always considerably more loss from that part of the seed which was never encapsulated but this was not regarded as serious since it did not affect the crystal and was insufficient to obscure vision by condensing out on the silica envelope and window of the puller.

Crystals were pulled at rates of from 5 mm to 5 cm/h. Those grown at the latter speed showed evidence of cell structure due to constitutional supercooling, while those grown at 10 mm/h and below did not. Crystal rotation was at 20 rev/min. A typical crystal is shown in fig. 1.

Samples were cut from crystals with a diamond wheel and/or a corundum/tungsten wire saw, and etched in the 1:1:1 $HCl:HNO_3:H_2O$ etch described by Miller *et al* [1] at ~80° C. Samples for electrical measurement were taken from material grown at 5 mm/h.

Measurements of conductivity and Hall coefficient were made in the temperature range 20 to 300° K using a cryostat described previously by Mitchell and Putley [10]. The samples were in the form of rectangular parallelopipeds, with platinum wires indium-soldered to the surface to form electrical connections. The voltages between the Hall probes and the conductivity probes were measured using a DC potentiometer.

Measurements were made on two samples cut from the same slice of the parent crystal. The surfaces of sample 1a were ground, and those of 1b were etched in a hot solution of 1:1:1 $HNO_3:HCl:H_2O$.

3. Results

The temperature dependence of the Hall coefficients of the samples is shown in fig. 2. The material is n-type, with an extrinsic carrier concentration, N_{ex}, of about $6 \times 10^{16}/cm^3$. This was calculated from the relation $N_{ex} = r/eR_H$ where r was assumed to be $3\pi/8$. The Hall coefficient in the extrinsic region rises slowly with $1/T$, and R_H was taken somewhat arbitrarily as the value at 70° K ($10^3/T = 13.5$). The variation of R_H with $1/T$ in the extrinsic region is probably mainly due to variation in r. It is concluded from the variation of mobility

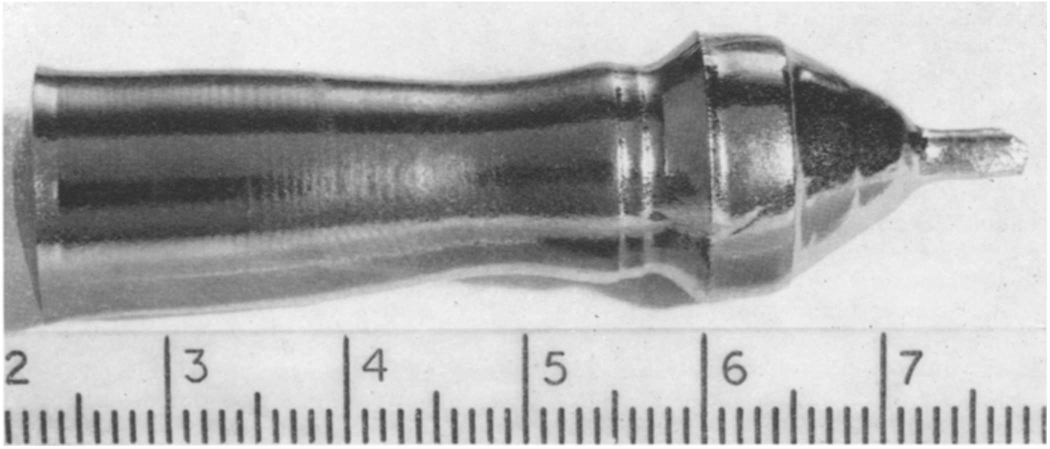

Figure 1 A pulled crystal of $PtSb_2$ (cm scale).

with temperature that the predominant type of carrier scattering is probably acoustic lattice scattering above 50° K, and ionised impurity scattering below 50° K, which could account for about a factor of two change in r.

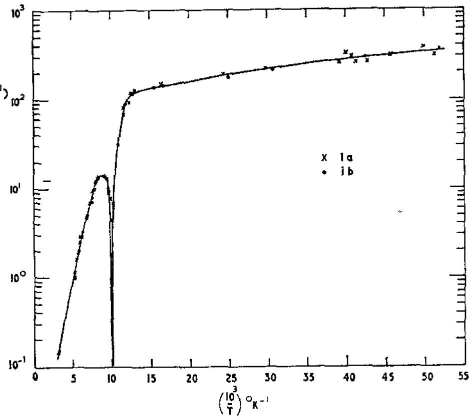

Figure 2 The absolute value of the Hall coefficient versus absolute temperature. R_H is negative to the right of $10^3/T = 10.2$, and positive to the left of this point.

The Hall coefficient changes sign at about 98° K and reaches a positive maximum at about 110° K. Therefore, in the intrinsic region the hole mobility exceeds the electron mobility. Anomalous reversals of the sign of the Hall coefficient can occur due to surface effects [11], but since two samples whose surfaces were subjected to quite different treatments follow almost identical curves, the behaviour in this case appears to be a property of the bulk material. Some relatively crude measurements were made at temperatures above room temperature which indicate that the sign of the Hall coefficient remains positive at least up to 500° K. The ratio of the hole mobility to the electron mobility, c, at the temperature of the Hall maximum, has been obtained as 1.77 from the relationship [11] $R_{\mathrm{max}}/R_{\mathrm{exh}} = (\mathrm{c}-1)^2/4\mathrm{c}$ where R_{max} and R_{exh} are the values of the Hall coefficient at the temperature of the Hall maximum and in the exhaustion region respectively. R_{exh} was taken as the value at 74° K.

The electrical conductivity of the samples as a function of temperature is shown in fig. 3. The two samples again follow almost identical curves.

The variation of electron mobility with temperature is shown in fig. 4. The points below 70° K were obtained by plotting $R_H\sigma$, and the points above 140° K were obtained from the conductivity and Hall coefficient data in the intrinsic region by solving the following equations for μ_e

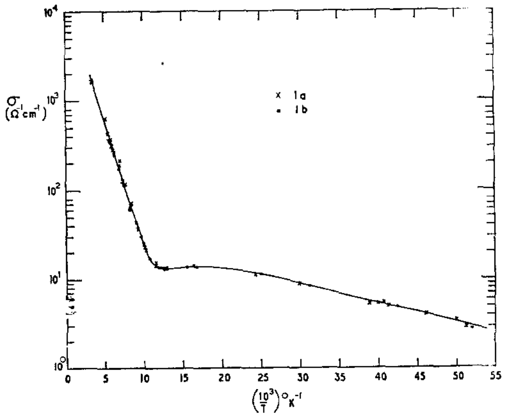

Figure 3 The electrical conductivity versus absolute temperature.

$$\sigma = en_i(1 + \mathrm{c})\,\mu_e$$

and
$$R_H = \frac{3\pi}{8e\,n_i}\left(\frac{1-\mathrm{c}}{1+\mathrm{c}}\right)$$

where n_i is the intrinsic carrier concentration and μ_e is the electron mobility. It is assumed that c is constant and the value calculated for 110° K was used. The mobility determined in this way is the conductivity mobility and in order to be consistent with the points plotted for temperatures below 70° K it is multiplied by $3\pi/8$. The mobility passes through a maximum of 2100 cm^2/V sec at about 50° K. The corresponding hole mobility would be about 3700 cm^2/V sec. At low temperatures the mobility varies approximately as $T^{\frac{3}{2}}$ which is consistent with the Conwell-Weisskopf formula [12] for ionised impurity scattering. At higher temperatures, the mobility varies as $T^{-\frac{3}{2}}$ which is consistent with acoustic lattice scattering [13].

A value of 0.112 eV for the thermal energy gap has been obtained from the slope of the log σ against $1/T$ curve in the intrinsic region. Assuming that the usual semiconductor equation for n_i may be applied, i.e.

$$n_i = \mathrm{A}T^{\frac{3}{2}} \exp\left(-E_g/2\mathrm{c}T\right)$$

where A is a constant, the conductivity is given by

$$\sigma = e\mathrm{A}(1 + \mathrm{c})\,\mu_e T^{\frac{3}{2}} \exp\left(-E_g/2\mathrm{k}T\right)$$

Thus since μ_e varies approximately as $T^{-\frac{3}{2}}$ the variation of σ with temperature is dominated by the exponential term.

A value for the thermal energy gap has also been obtained from a plot of ln $R_H T^{\frac{3}{2}}$ against

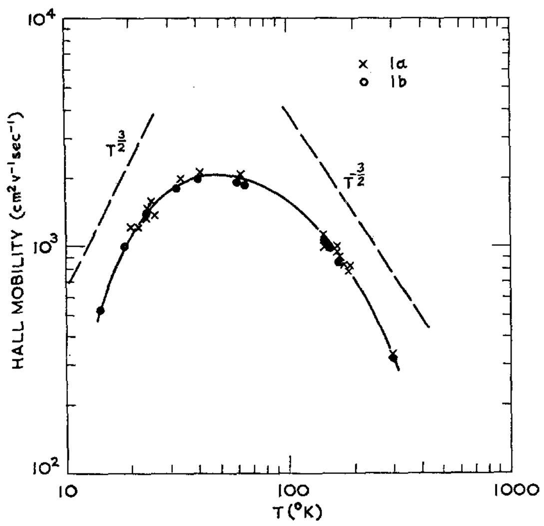

Figure 4 The electron Hall mobility versus absolute temperature. Points to the left of 74° K were obtained by plotting $R_H \sigma$. Points to the right of 140° K were obtained from the conductivity and Hall coefficient data in the intrinsic region as indicated in the text. The broken lines indicate slopes of $+\frac{3}{2}$ and $-\frac{3}{2}$.

$1/T$ [13]. The slope could be determined less accurately from this graph than from fig. 3. Within the limits of the accuracy, however, the value obtained agrees with the value given above.

4. Discussion

It is evident that the liquid encapsulation technique effects a considerable improvement in the quality of pulled crystals of $PtSb_2$. The value obtained for the intrinsic energy gap is higher than that reported previously (0.075 eV) by Miller *et al* [1]. However, the material used by Miller *et al* had much higher carrier concentrations than that used in the present investigation, and intrinsic behaviour was not observed below about 700° K. The analysis of the data was therefore complicated by the fact that the material was degenerate, and assumptions were made about the variation with temperature of the energy gap, the carrier mobilities, and the density of states effective masses, which may have been invalid. They also observed that the Hall coefficient in the intrinsic region was negative, the ratio of electron to hole mobility being close to 1. The Seebeck coefficient was also small and negative. This is not necessarily inconsistent with the present investigation, since c will depend on temperature if the bands are non-parabolic, or if either electrons or holes are distributed between bands with different effective masses.

It seems probable that further improvements could be effected by purification either of the elements or of the compound. The zone refining of Pt should present no difficulty and might have the effect of removing other Pt group metals, but it would be better if the compound itself could be zone refined before pulling. To be fully effective, this should also be done by a liquid encapsulation technique, both to preserve stoichiometry, and to prevent the redistribution of volatile impurities. We have not attempted this and such a process has not, to our knowledge, been reported*.

Acknowledgements

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*Liquid encapsulated zone refining has, in fact, been reported since this paper was submitted [E. M. Swiggard, *J. Electrochem. Soc.* **114** (1967) 976].