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Growth and Properties of $Cd_xHg_{1-x}Te$ Crystals

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It has been found that there are two main factors complicating the preparation of $Cd_xHg_{1-x}Te$. The marked difference between the liquidus and solidus curves of the CdTe—HgTe pseudo-binary system gives the expected problems of segregation of CdTe with respect to HgTe during growth but there are also problems due to the segregation of any excess Te in the melt. A 2% excess of Te can give rise to pronounced constitutional supercooling effects. To avoid this, careful control of melt stoichiometry is required. This is made difficult by the high vapour pressure of mercury over the melt, the value of which is not known with great accuracy.

The conditions of melt stoichiometry required for crystal growth do not necessarily give material of the required type and resistivity and this must be adjusted after growth by annealing at a controlled mercury pressure at a fixed temperature.

1. Introduction

The system HgTe—CdTe was first studied by Lawson *et al* [1] who showed that HgTe formed a continuous series of solid solutions with CdTe. They also showed that the energy gap of the series varied between that of CdTe (1.5 eV) and zero for solids containing a high percentage of HgTe. HgTe is, in fact, a semimetal. Much work has been published since on the properties of CdHgTe and has been reviewed by Harman [2]. There is, however, little description in the literature of the method used for the preparation of the material. In the present work an attempt has been made to carry out a systematic investigation of the conditions of preparation, and to develop a simple reproducible method for the preparation of homogeneous crystals. Most emphasis has been placed on the preparation of material in the composition range, 35 mole % CdTe to 15 mole % CdTe, as this yields a semiconductor with a small energy gap which is useful as a photoconductor. For this application it is necessary to be able to control: (1) the energy gap; (2) the alloy structure; (3) the resistivity.

These three variables all depend upon the conditions of growth of the material.

2. Factors Affecting Crystal Properties

The form of the pseudo-binary diagram of CdHgTe, given by Blair and Newnham [3], shows that at a growth interface at equilibrium there will be considerable segregation of CdTe with respect to HgTe, due to the widely separated liquidus and solidus lines. At a high growth speed this will give rise to non-equilibrium growth. Non-equilibrium growth can result in the production of non-uniform material on a macroscopic scale. In extreme cases, constitutional supercooling (csc) will occur and this will give non-uniformity on a microscopic scale. Any subsequent heat treatment of such material will result in a redistribution of the component in excess. In CdHgTe there is also the possibility of csc occurring in the metal-Te system. The probability of this is increased by the high volatility of mercury and consequential deviations from stoichiometry in the melt. If deviations from stoichiometry occur this may result in changes in the level of electrically active defects in the crystal.

The velocity, V, at which csc becomes apparent is given by Tiller [4] to be

$$V = \frac{GD\mathrm{k}}{C(1-\mathrm{k})m}$$

where C is the concentration of solute in the solid, k the segregation coefficient, m the liquidus slope, G the temperature gradient in the melt, and D the diffusion coefficient in the melt.

In the case of CdHgTe, G is the same for both the CdTe segregation with respect to HgTe and for segregation of excess Te. Typical values are:

(a) for excess Te segregation $m = -10^\circ$ C per %

$$C = 4\%$$

since k is about 0.1, $1 - k \triangleq 1$

$$V_{Te} = 1/400 \times D_{Te}$$

(b) for CdTe segregation $m = 3^\circ$ C per %

$$C = 20\%$$

since k is about 3, $1 - k = -2$

$$V_{Cd} = 1/40 \times D_{Cd}.$$

Thus $V_{Cd} > V_{Te}$ even if the diffusion coefficients for the two species are equal. It seems likely that $D_{Cd} > D_{Te}$ since the Cd ion is considerably smaller than the Te ion. It, therefore, seems reasonable that the Te might cause csc before the Cd and in practice this appears to be the case.

3. Experimental Preparation of Material

A preliminary investigation was carried out to determine the problems involved in the preparation of CdHgTe, in particular, the vapour pressures over melts and whether zone refining is practicable. Experiments were carried out with melts of several HgTe to CdTe ratios and the melting points determined under various mercury vapour pressures. The maxima of the melting point versus Hg pressure plots obtained, were taken to correspond to stoichiometric melts. It was assumed that the vapour pressures of Cd and Te were small compared with the Hg pressure over the melt. Results confirmed the value given by Rodot [5] for the vapour pressure over stoichiometric HgTe of 15 atm, and also showed that melts containing up to 25 mole % CdTe had approximately the same vapour pressure. An apparatus was constructed to zone refine CdHgTe under a Hg vapour pressure of 15 atm. The first experiments showed that there are two difficulties: (a) there was rapid alloying of the part of the bar which had already been grown, by the mercury vapour (this has already been observed by Harman [6] in the case of pure HgTe); (b) there was evidence of non-equilibrium growth, which, in subsequent experiments, was shown to be due to growth at too high a speed.

Consideration was given to a liquid encapsulation technique, but as a suitable crystal puller was not available, it was decided to concentrate on the vertical Bridgman method of growth.

The starting materials for the preparation are Johnson Matthey 1st quality Hg and Cominco 69s, Te and Cd. The calculated quantities of the three elements are weighed out and sealed under vacuum into a silica crucible. It has not been found necessary to vacuum distil the constituent elements into the crucible in order to prevent contamination but it is necessary to prevent the Hg and Cd coming into contact with each other during the loading process since the amalgam formed readily oxidises. The oxide causes the crystal to stick to the crucible during growth. The compound is formed by heating the crucible and contents slowly from about 450° C to 50° C above the relevant liquidus temperature of the alloy. If the process is carried out over a period of about 1 week for a melt of 800 g there is no problem with explosion due to uncombined quantities of Hg. Attempts were made to study the effect of various surface treatments on the inside surface of the crucible, e.g. carbon coatings, flaming etc, but it was concluded that the best surface was that of the original silica.

A conventional Bridgman furnace was used with a steep temperature gradient (100° C/cm) being set up between the furnace and a water cooled coil. Crystals were grown at speeds ranging from 1 cm/h to 0.25 mm/h using different melt compositions and it was found that the behaviour was very greatly dependent upon these two factors.

4. Segregation Effects in CdHgTe

As has been mentioned above there is the possibility of csc arising due both to segregation of CdTe with respect to HgTe and segregation of any excess Te in the melt. This latter effect would appear to be the more critical. The magnitude of the effect has been studied in crystals of differing compositions grown at different speeds. Slices cut perpendicular to the direction of growth of the crystals were mechanically polished and then etched to reveal dislocation etch pits. Fig. 1 shows the effect of growth on the structure of HgTe grown from melts containing 2% excess Te. It is seen in 1a that at 2.5 mm/h there are large inclusions in the material. Electron microprobe analysis has shown these to be droplets of Te, formed during the process of csc.

At speeds in the range 2.5 mm/h to 0.5 mm/h a mosaic of dislocation etch pits is formed. 1b

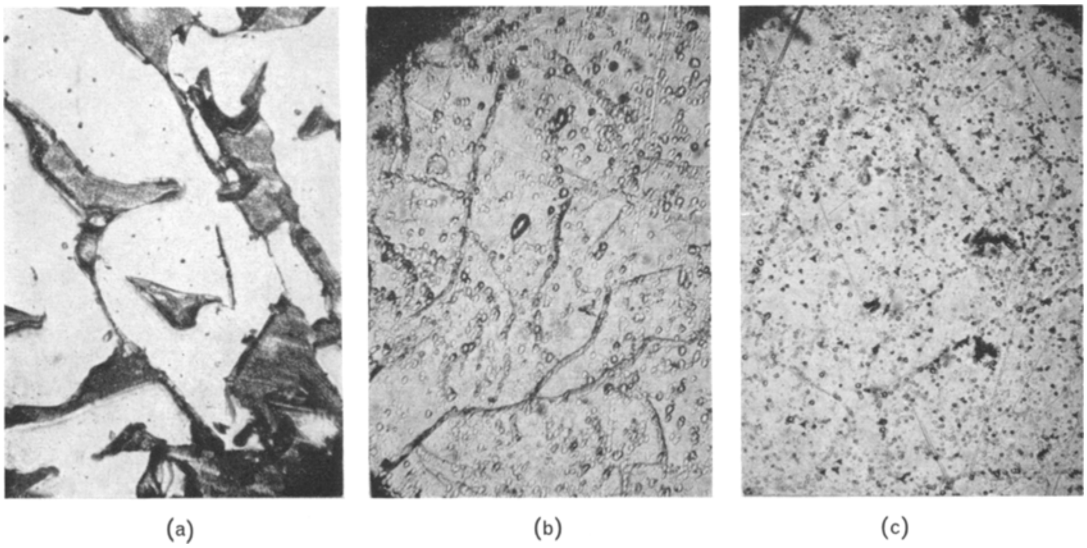
(a) (b) (c)

Figure 1 Effect of growth speed on the mosaic structure in HgTe. (a) 2.5 mm/h, (b) 0.50 mm/h, (c) 0.25 mm/h.

shows a crystal grown at 0.75 mm/h. At a speed of 0.25 mm/h as in 1c the mosaic effect is less apparent. Similar effects are seen in alloys grown from melts containing 20 mole % CdTe and a small excess of Te. The mosaic structure has also been examined by electron probe analysis but it has not been possible to show that the boundaries of the mosaics are rich in Te. There can be little doubt, however, that this is the case.

It is apparent that to avoid csc due to excess Te it is necessary to control the stoichiometry of the melt to better than 2% since it is not practical to reduce the growth speed to less than 0.25 mm/h in order to improve segregation.

Fig. 2 shows the effect of adjusting the Hg to Te ratio in HgTe with crystals grown at 0.75 mm/h. 1a is from a crystal in which the composition of the melt has been made as near stoichiometric as possible by adjusting the contents of the crucible to allow for loss of Hg into the space above the melt. This crystal shows very little mosaic effect. 1b shows a crystal grown from a

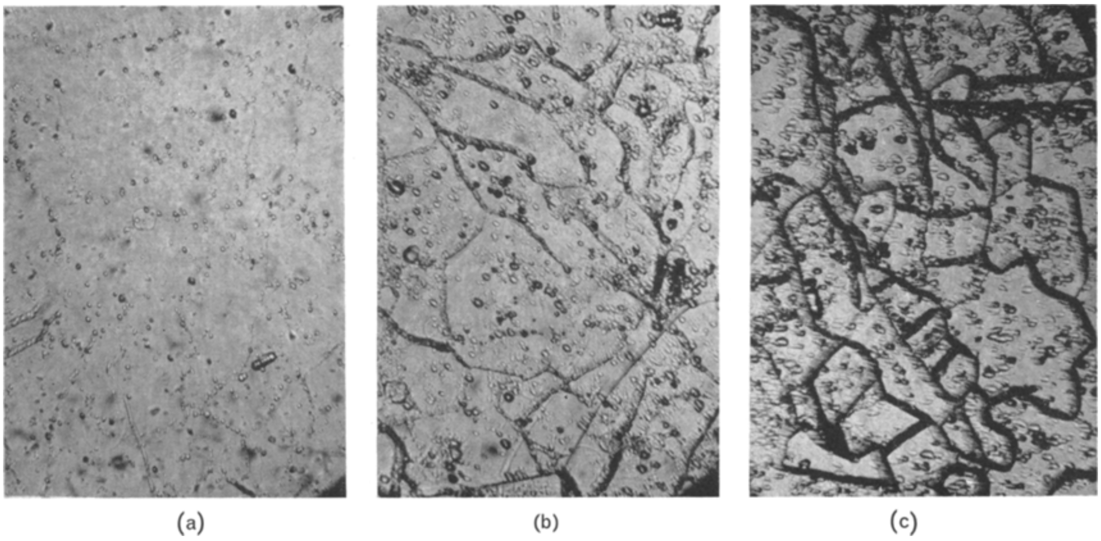
(a) (b) (c)

Figure 2 Effect of composition on the mosaic structure in HgTe. (a) stoichiometric, (b) 4% excess Te, (c) 12% excess Te.

melt containing 4% excess Te and 1c a crystal grown from a melt containing 12% excess Te. Both 1b and 1c show pronounced effects of csc. The observations at 12% excess Te are not in agreement with those of Delves [7], who suggested that at this composition there was a phase containing two immiscible liquids from which growth could take place without csc.

It is clear that the ratio of metal to Te in the melt is extremely critical, in order that csc should be avoided even at very low growth speeds. Adjustment of the stoichiometry of the melt entails an accurate knowledge of the equilibrium vapour pressure of Hg over the melt in order that the excess Hg required to compensate for loss from the melt into vapour can be calculated. The adjustment is made difficult since in general the CdTe to HgTe ratio varies along a bar and the equilibrium Hg vapour pressure therefore varies. There may therefore be varying deviation from stoichiometry along the bar.

The segregation of CdTe with respect to HgTe has been studied over the speed range 1 cm/h to 0.25 mm/h. Fig. 3 shows the composition profiles of three crystals with initial melt composition of 20 mole % CdTe when grown at speeds of 2.5, 0.5 and 0.25 mm/h. It is seen that there is little segregation at high speeds but pronounced segregation at slow speeds. At high growth speeds the effective segregation coefficient (k) approaches 1. This is due to the Burton and Slichter [8] mechanism giving rise to a layer depleted in CdTe at the solid liquid interface. Any stirring in the melt will modify the depletion layer and will thus alter the effective k. Since stirring by convection is unlikely to be constant across the whole interface, due to non-symmetry of isotherms in the furnace, there will be local variations in k and hence composition. At low speeds growth approaches equilibrium condition, when there will be no depletion layer and therefore no local variations in composition. Measurement of the energy gap of crystals grown at slow speeds shows them to be more uniform than crystals grown at high speeds.

In crystals grown at 0.5 mm/h from melts containing a correctly adjusted metal to Te ratio there is no evidence of mosaics caused by csc due to the CdTe to HgTe segregation. This speed is used for the routine preparation of crystals.

Since the composition of slow grown crystals varies along its length, the composition of the initial melt is chosen to obtain the maximum quantity of material of the required composition.

5. Control of Resistivity of CdHgTe

In CdHgTe the resistivity of the material is controlled in the extrinsic region, not by the presence of foreign elements but by defects in the lattice. The CdTe rich end of the grown crystal is p-type, the acceptor concentration falling as the CdTe percentage falls. At the end of the crystal with CdTe compositions less than 20 mole % the material becomes a semi-metal. The concentration of electrically active centres in the crystal can be varied by altering the stoichiometry of the melt. Additions of Hg tend to make the crystal more n-type at a given composition. Thus, the stoichiometry of the melt influences the doping of the crystal. This method is not satisfactory for good control since changes will occur in the number of defects present in the lattice

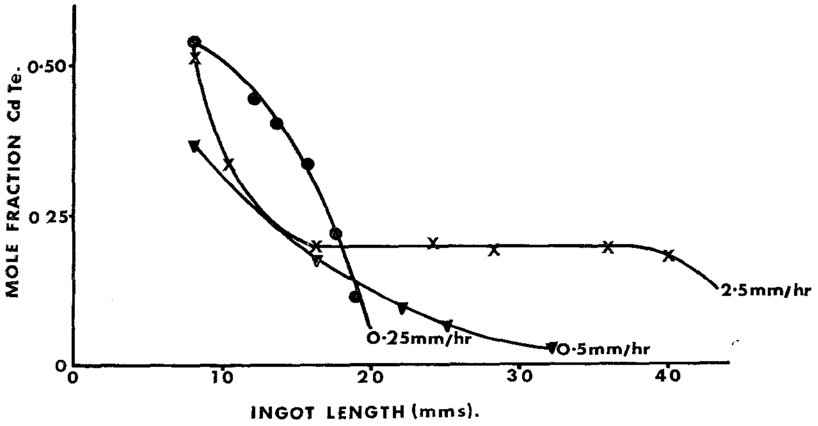

Figure 3 Segregation effects in $Cd_xHg_{1-x}Te$ due to growth speed.

as the crystal is cooled to room temperature and this process is unlikely to be reproducible.

Annealing of CdHgTe under an uncontrolled Hg pressure has little beneficial effect since it may result in a loss of Hg from the surface of the material. If there are any non-equilibrium concentrations of the constituent elements, e.g.Te in the mosaic structure of the crystal, annealing will result in the redistribution of this element.

Control of resistivity can be achieved by annealing CdHgTe at a particular temperature under a controlled mercury vapour pressure. Rodot [5, 9] has published many results for HgTe and $Cd_{0.07}Hg_{0.93}Te$, which are semi-metals, and a few results for $Cd_{0.25}Hg_{0.75}Te$ which is a semiconductor. We have concentrated our experiments on alloys containing more than 20 mole % CdTe. A typical result is shown in fig. 4 for $Cd_{0.25}Hg_{0.75}Te$. Curves 4a and 4b show the variation of 77° K carrier concentration (determined by Hall measurement) with mercury pressure at annealing temperatures of 300 and 400° C respectively. Fig. 5 shows the variation of 77° K resistivity with mercury vapour pressure.

An alloy of CdHgTe is therefore prepared from a melt whose stoichiometry has been adjusted to obtain good quality crystal; if the material obtained does not have the required resistivity this can be adjusted afterwards by annealing at a fixed temperature under a suitable mercury vapour pressure.

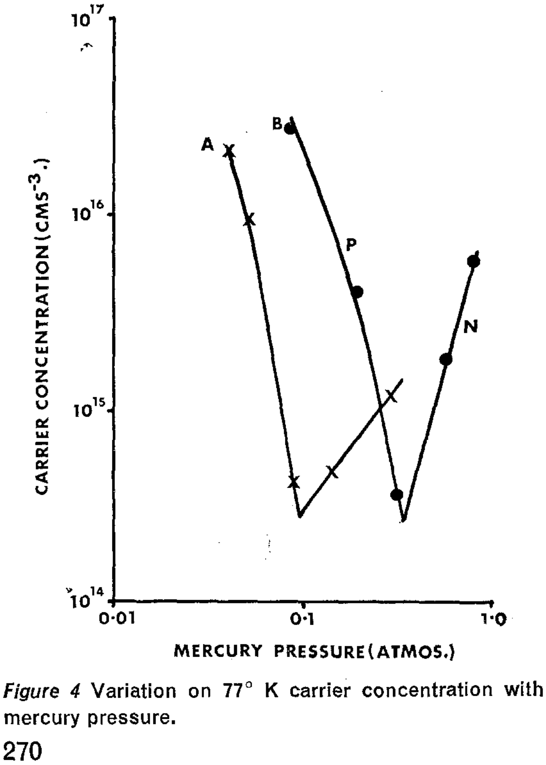

Figure 4 Variation on 77° K carrier concentration with mercury pressure.

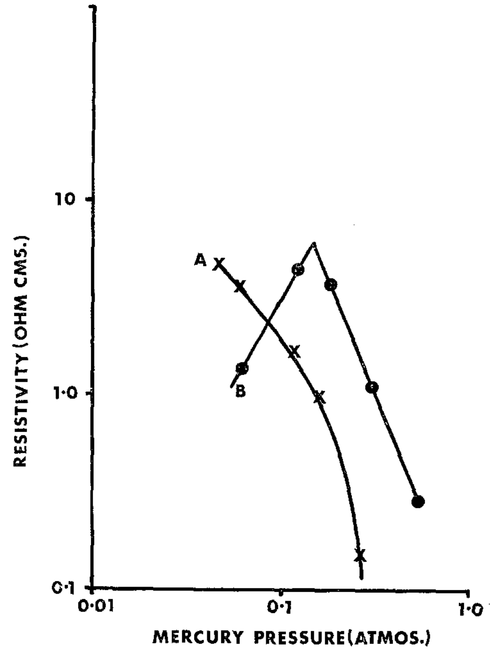

Figure 5 Variation of 77°K resistivity with mercury pressure.

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