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Section I.1 : Crystal Growth.

THE MELT-GROWTH AND CHARACTERIZATION OF CADMIUM TELLURIDE

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Résumé. — Dans cet exposé on passe en revue les différentes méthodes de croissance de tellurure de cadmium à partir de bains fondus. On s'intéressera plus particulièrement aux techniques de contrôle de la pression de dissociation. Les avantages potentiels d'une compensation de pressions sont considérés simultanément aux premiers résultats obtenus par une croissance sous encapsulation liquide. La caractérisation des cristaux tirés sous encapsulation liquide nécessite une étude des principaux défauts physiques, des impuretés et des associations impuretés-défauts. On s'intéressera à l'origine de ces perturbations et on proposera des solutions en vue de leur contrôle, voire leur élimination.

Abstract. — Developments in the melt-growth of CdTe are reviewed particularly with respect to techniques for controlling the dissociation pressure. The potential merits of Pressure Balancing are considered together with the results of a preliminary LEC growth investigation. The characterization of the LEC crystals involves a survey of the main defects-low angle grain boundaries, twins, dislocations, precipitates, impurities and impurity defects-together with a discussion on their origin, and experience and suggestions for their elimination or control.

1. Introduction. — In reviewing developments in the melt-growth of CdTe the main considerations will assess the field of stoichiometric or near-stoichiometric growth although some pertinent aspects of solution growth will be considered. The main emphasis will be on the LEC-growth of CdTe and the characterization of the pulled crystals.

The growth of any large single crystal semiconductor with predetermined properties is an ultimate goal for most crystal growers. The slow painstaking struggle against capricious odds is like following a mirage. Cadmium telluride is no exception to this pattern, and, whilst impressive strides have been made in improvements in the quality and perfection of crystals in the last few years the ultimate goal is not yet within the grasp of the crystal grower. One uncontrollable obstacle is unfortunately the device man who constantly moves the goal.

A good cross-sectional view of the state of development of the melt-growth of CdTe was presented at the last symposium by various authors including Strauss [1], Kyle [2], Triboulet [3] and Vandekerckhof [4]. The splendid review by Strauss [1] analysed the closed tube technologies, both horizontal and vertical with and without a Cd reservoir, for the melt-growth of CdTe. A detailed re-examination of these procedures is not therefore necessary here. The main physico-chemical aspects of CdTe will however be considered in order to set in perspective the problems of growing CdTe and also to provide a framework for discussing LEC growth and for considering the possibility of an

alternative technique, Pressure Balancing [5]. This latter dormant technique has conceptually appealing characteristics for the growth of CdTe.

2. The pressure problem. — The melt-growth of CdTe is normally carried out in a regime where solid CdTe separates from a homogeneous liquid phase of Cd plus Te which is in substantial equilibrium with a mixture of Cd and Te vapours. According to the phase rule the system is univariant and one parameter such as the temperature (an independent parameter) completely determines the system. The significance of this for the growth of CdTe can be seen from the phase relationship that was reported by Strauss [1] and is reproduced here as figure 1. Two dependent parameters, the Cd and Te partial pressures, are plotted on the same graph as a function of the reciprocal temperature. At the maximum melting point the partial pressures of Cd and Te are respectively ~ 0.7 atm and $\sim 5 \times 10^{-3}$ atm. Thus to achieve growth under near equilibrium conditions it would be necessary either *a)* to maintain a Cd vapour pressure over the melt of ~ 0.7 atm by using a Cd reservoir at ~ 728 °C and also to ensure that the vapour did not contact any surface having a temperature less than ~ 728 °C or *b)* to use a completely sealed system where the containing wall temperatures were not less than ~ 728 °C ie using so-called hot-wall technology. There is a minimum constraint for the Te pressure which would be satisfied by the Cd constraint noted above. Working at significantly higher or lower pressures of Cd constitute

FIG. 1. — Cd and Te partial pressures as a function of $1/T$ for solid-liquid-vapour equilibrium in the Cd-Te system (after Strauss ref. [1]).

solution growth. Here one could engender constraints of constitutional supercooling which is not a featured topic for this paper.

3. Experimental solutions of the pressure problem. — Growth techniques fulfilling the above fundamental constraints have been developed and are illustrated in figure 2. The vertical and horizontal Stockbarger and Bridgman techniques are illustrated diagrammatically as 2a and 2b. They are classic solutions of the hot wall and Cd reservoir technologies noted above. The pulling technologies are depicted in figures 2c and 2d. In figure 2c, which represents the Liquid Encapsulation technique a layer of encapsulant floating on the surface of the melt effectively provides a hot wall. This layer acts as a liquid seal provided the inert gas pressure on the surface of the encapsulant is greater than the dissociation pressure of the melt (~ 0.7 atm). Successful experimental practice will be discussed later: it normally requires pressures considerably in excess of the dissociation pressure.

The method of LEC-growth involves a post-crystallization situation in which the solid cools down whilst

coated by a thin film of encapsulant—assuming ideal conditions hold. Thus the solid cools in a constant composition environment. This is a desirable feature in certain circumstances. But, there are situations for II-VI compounds in general and for CdTe in particular where the ability to grow and cool down the crystal under a known easily-adjustable pressure of Cd or Te is needed. A growth technique that also makes use of the undoubted virtues of crystal pulling involving unconstrained growth from a stirred melt would be highly advantageous. In principle Pressure Balancing [5] can be adapted to a pulling mode and is designed to have an independent pressure control facility.

A diagrammatic representation of the pressure balancing apparatus is shown in figure 2d. The crystal is pulled from a melt contained in the inner envelope or growth chamber 9 which is supported and surrounded by the main pressure chamber 7. The pull rod passes through a normal seal in 7 and then through a liquid seal 18 contained in a well in the pull rod bearing seal block 8. The nub of the technique is the means for maintaining the liquid seal in position. It is prevented from running down the pull rod under the action of gravity by the screwing action of the pull rod against a female screw thread 19 cut out of the hole in the bearing seal block 8. Any liquid between the rod and the thread is screwed back as in an Archimedes screw into the well, provided the rotation is in the upward sense. The liquid seal prevents diffusive loss of volatile species where the pull rod enters the growth chamber. Mechanical loss of volatile species by pressure differentials across the liquid seal is prevented by Pressure Balancing.

Pressure Balancing can be effected automatically by the two way bubbler 17 or by inert gas pressure regulation. In the latter case the cold growth chamber 9 is first evacuated. The system is then sealed by heating the encapsulant with the built-in heater situated in the pull rod bearing block. The charge is gradually heated and as the pressure p_g in the growth chamber tends to rise, the pressure rise is sensed by the liquid level sensor 16. This sensor controls the valve 15 which can admit or release inert gas to or from the growth chamber. The pressure p_0 in the outer vessel 7 is thus automatically controlled to balance p_g . The heater 13 can by suitable design be made to control the minimum temperature in the system, that is the temperature of the reservoir of the volatile species (Cd). Thus in principle by regulating the reservoir temperature 13 one can control the pressure of the Cd in the environment during crystal growth and in the post-crystallization period. Furthermore one could readily record the actual vapour pressure of the Cd used during and after crystal growth.

This technique has been applied successfully to the growth of GaAs. Its further development has been somewhat curtailed by the availability of the simpler LEC technology. The advantage of having independent pressure control would seem to merit a reconsideration of the use of Pressure Balancing for CdTe.

FIG. 2. — Techniques suitable for the growth of CdTe. a) Stockbarger/vertical Bridgman technique illustrating hot wall technology where the sealed tube is maintained at a temperature $\sim 728^\circ\text{C}$ by heater 2. The diagram depicts a zone pass modification of the original Stockbarger process which is strictly a normal freeze process. b) Cd reservoir technique where the Cd, 6, is maintained $\sim 728^\circ\text{C}$ for stoichiometric growth. c) LEC growth — conventional pulling with encapsulant 4. d) Pressure Balancing — described in text.

4. Defects and the width of the solid phase field. —

There is ample evidence [6-9] that the properties of CdTe are influenced if not controlled by the chemical and thermal environment in the period following crystallization. Before discussing LEC-growth it is necessary to consider the potential concentration of defects which can be introduced into CdTe. There is a reasonable case for believing that the concentration and nature of defects are such that they actually influence the mode of crystal growth itself.

The most definitive early study that proposes a model for the solid phase field of CdTe is that of de Nobel [6]. This model was based on the vapour pressure data for Cd over CdTe and assumed the existence of various defect species. It showed a maximum solid phase width ~ 10 ppm. It is appropriate to consider alternative perhaps more direct ways for revealing the magnitude of the solid phase width in CdTe. A combination of lattice parameter and density measurements is certainly more direct although even here there are problems of interpretation. It is possible nonetheless to show that the potential defect concentration in melt-grown CdTe crystals is very much greater than is indicated by de Nobel's model.

It is interesting to contrast the situation in CdTe with that in GaAs. Studies [10, 11] involving a systematic survey of very precise lattice parameter measurements on GaAs crystals that were grown by different methods have been made using an Apex system [12]. It was found possible to reproducibly measure the lattice parameter to one part per million (ppm), or to a factor of ten better if special precautions were taken. Since various phenomena indicate that the native point defect concentration in GaAs is of the order of 10^{19} defects per cm^3 at the melting point it is in principle possible to compare GaAs grown at high temperatures (m.pt $1\,237^\circ\text{C}$) with GaAs grown epitaxially at low temperatures (750°C - 850°C). The point defect concentration in epitaxially-grown GaAs would be expected to be orders of magnitude lower than in melt-grown crystals. The experimental results however showed that there was no difference in the lattice parameter of undoped GaAs specimens taken from crystals grown either from the melt, from Ga solution or from the vapour phase. The mean value representing each growth technique was $5.653\,25 \pm 0.000\,02$ at 27°C . Driscoll and Willoughby [13] have also shown that GaAs specimens that were rapidly chilled from $1\,164^\circ\text{C}$ to room temperature did show a 28 ppm increase over the standard lattice parameter but this deviation reduced to near zero in about 72 hours. It is argued that this lattice dilation is caused by Frenkel defects in the As sub-lattice [13, 14]. This evidence might also indicate the presence of Ga Frenkel defects.

Lattice parameter measurements [2, 15-17] on CdTe show a different pattern of behaviour to those on GaAs. The results of measurements by Kiseleva *et al.* [15] and by Kyle [2] show large (> 100 ppm) apparently

permanent differences in the values of the lattice parameter for CdTe prepared by different methods. These differences are however larger than those recently reported by Vaipolin *et al.* [17]. Kiseleva *et al.*'s results showed an apparent correlation of the measured lattice parameter with the free carrier concentration found in samples. Further, the difference in density obtained from weight measurements and X-ray measurements was used to deduce vacancy concentrations in high n and p type material. These concentrations were 2.0 and 5.7×10^{19} per cm^3 respectively. This method of interpretation relies on differences between two almost equal quantities that stretched the measurement accuracy of experimental and fundamental parameters to the limits. That vacancies should contract the lattice parameter is questionable. There are contrary viewpoints [18, 19] but it is not the purpose of the present paper to discuss those here. An alternative simpler way of looking at the results and one that gives a useful guide to defect density differences is to normalise the lattice parameter deviations in units of $\Delta a/a_0$ where a_0 is a convenient reference value. A vacancy or interstitial is unlikely to reduce the lattice parameter by more than one normalised lattice parameter (NLP) unit or increase it by more than a few NLP units at the most. Values of $\Delta a/a_0$ can thus be used to compare defect density differences with a view to assessing the order of magnitude of the maximum phase width. Further since there are likely to be positive and negative deviations associated with different defects $\Delta a/a_0$ will probably underestimate defect density differences and hence phase widths from suitably selected material.

Kiseleva *et al.* [15] and Kyle's [2] results are shown in table I. It is misleading to compare the results by the various authors for any one method of preparation since the exact method of preparation particularly the thermal histories are probably not comparable. It seems at this stage of our understanding worth establishing the extremes of lattice parameter difference found by the various authors.

The maximum NLP difference found by Kiseleva *et al.* [15] was 602 ppm between a Bridgman-grown crystal and a crystal grown from excess Cd. In Kyle's [2] experiments the maximum NLP difference was 448 ppm between crystals grown from Cd and Te solutions. Vaipolin *et al.* [17] however considered that their lattice parameter measurements on variously-grown CdTe were the same within experimental error. His mean value of $6.481\,8 \pm 0.000\,3$ would thus indicate a maximum variation of less than 100 ppm in the NLP. Nevertheless a larger NLP difference can be seen in the extreme values recorded in his results. If one unit of lattice parameter gave rise to one defect and say one free carrier, then, the maximum deviations found by the respective authors Kiseleva *et al.* and Kyle would be 1.7 and 1.3×10^{19} NLP defects or carriers per cm^3 . Such large NLP defect density differences clearly support a view that the maximum solid phase width in

TABLE I

Effect of growth conditions on the lattice parameter of CdTe

Growth technique	Growth environment	Lattice parameter (Å)	$\Delta a/a_0$ (**) in ppm	Reference
Bridgman	Cd (*), 730 °C ~ 0.7 atm	6.480 2	+ 31	(^a)
Bridgman	Cd (*), 800 °C ~ 1.5 atm	6.484 0	+ 617	(^a)
Bridgman	Cd (*), 845 °C ~ 2.3 atm	6.480 3	+ 46	(^a)
Bridgman		6.480 5	+ 77	(^b)
Solution	xs Cd 850 °C	6.480 1	+ 15	(^a)
Solution	xs Cd	6.479 4	– 93	(^b)
Solution	Te-rich	6.482 3	+ 355	(^b)

(*) Cd reservoir temperature.

(**) Δa = measured lattice — a_0 where $a_0 = 6.480\,0\,\text{Å}$ (arbitrary reference).(^a) Ref. [17].(^b) Ref. [2].

CdTe is at least an order of magnitude greater than originally suggested by de Nobel. But, more precise measurements on equilibrated specimens with known thermal histories will be needed to fully substantiate this implication.

5. Liquid encapsulated growth. — Meiling and Leombruno have reported attempts at the LEC-growth of CdTe. In an abstract account [20] of their work they reported great difficulty in growing crystals larger than 5 mm in diameter. This was attributed in part to the poor thermal conductivity ($0.058\,0\,\text{W cm}^{-1}\text{ deg}^{-1}$ at $32.7\,^\circ\text{C}$ (21)) of CdTe. Vandekerckof [4] also reported this problem. Additionally, he found difficulties with Cd loss from the periphery of the crystal and with discoloration of the B_2O_3 . Klausutis *et al.* [21] however were able to grow polycrystalline boules of $\text{CdTe}_{1-x}\text{Se}_x$ (x from 0.05 to 0.15) without either of the above difficulties. They grew their crystals using an over-pressure of 20 atm of Ar in their pulling chamber. But, they noted Cd vapour losses occurred below a pressure of 13 atm. In the authors' experience with CdTe, vapour losses occurred when the pressure fell below ~ 5 atm.

In the present investigation the procedure for optimising the growth conditions to obtain control of diameter of the crystals was found to be more critical and time consuming than for example the equivalent procedure for GaAs or InP. This was a consequence of the lower temperature gradients which develop in the solid at the solid-liquid interface with CdTe compared with GaAs or InP. The ratio of the thermal conductivity of CdTe to that of GaAs for example is ~ 0.11 at room temperature and ~ 0.35 at their melting points.

In almost all the pulls to date the B_2O_3 layer remained either perfectly clear (most cases) or adequately clear. In the case of the III-V compounds [22] poor visibility is generally attributed to traces of water in the B_2O_3 and fairly stringent control of the preparation of

B_2O_3 is necessary to overcome this problem [23]. But there is likely to be more than one cause of cloudiness. Prolonged contact of the molten elements Cd and Te with B_2O_3 in the process of forming the compound (see below) has been found to cause cloudiness of the B_2O_3 .

Most of the crystals were prepared in two stages. In the first stage appropriate amounts of Cd and Te were reacted together under B_2O_3 under a pressure of ~ 27 atm N_2 gas. After cooling down, the CdTe was extracted by dissolving the B_2O_3 with hot distilled water. In the second stage, the pulling procedure, the etched and dried preformed-charge of CdTe was placed in a silica crucible and covered with B_2O_3 pellets. The seeds used initially were polycrystalline sections of preformed or prepulled crystals. Later, single crystal sections from CdTe prepared by the solvent evaporation process [24] were used. The charge was melted down and the seeding and growth carried out in the conventional manner. The pull rates were typically $0.5\,\text{cm per hr}$ and the seed rotation rate was 10 rpm. Crucible rotation was not used. Reasonably-shaped crystals could be obtained by manual control but the crucible position relative to the coil was very critical. The depth of B_2O_3 was a compromise. Too shallow a depth resulted in an inadequate layer of B_2O_3 being drawn up with the crystal, resulting in Cd loss from the surface of the pulled crystal. Too great a depth produced characteristically bulbous shaped crystals whose diameter gradually increased and decreased in a periodic manner. In the equivalent situation in GaP Nygren [25] has shown that the repeat period correlates with the depth of B_2O_3 . A thickness of B_2O_3 around 7 mm permitted adequate control of crystal diameter. Completely single crystals have not yet been grown, although occasionally almost the whole of the crystal section was single with three or four boundaries just at the edge of the section. Examples of LEC crystals are

FIG. 3. — Two LEC-CdTe crystals showing. *a*) Necking procedure (left crystal). *b*) Bulbous growth (see text) followed by reasonable diameter control.

shown in figure 3. The current state of the art then is one of characterising the crystal defects identifying their causes, and developing procedures for preventing them.

6. Crystalline defects and their characterization.

— 6.1 BOUNDARIES, TWINS, DISLOCATIONS AND PRECIPITATES. — *Boundaries.* — The major visible defects were boundaries which separated individual single crystal grains. They were generally visible on the outside of the crystals. The separate single crystal regions were easily identified by viewing a lightly-ground and obliquely-illuminated surface under a low magnification binocular microscope. The tiny cleavage planes in each single crystal grain produced marked contrast changes in the reflected light intensity as the specimen was gradually rotated. Suitable etches like 1 vol 48 % HF : 3 vols conc HNO_3 : 4 vols 2 % aqueous AgNO_3 [26] could equally produce good visible contrast between grains. Figure 4 shows an example of a section of a crystal of quite poor crystalline quality.

Two types of boundary were identified, low angle grain boundaries and twin boundaries. The presence of low angle grain boundaries is very significant. Back-reflection Laue photographs taken from the surfaces adjacent to low angle boundaries showed that the angle of misorientation was less than a degree. The twin boundaries are very distinct in that *a*) they appeared to be almost always lamellar twins and *b*) they intersected the cut surfaces in parallel lines and were thus readily

FIG. 4. — Etched cross-section of a poor LEC-crystal showing low angle grain boundaries and lamellar twins.

distinguishable from low angle grain boundaries which gave curved intersections. Examples of both low angle grain boundaries and twins can be seen in figure 4.

Twins. — The twin boundaries are apparently always of the lamella variety [27], that is they appear to originate and propagate in pairs. Interesting examples can be seen in figure 5 where the direction of inter-

FIG. 5. — Photomicrograph of a section of an LEC crystal showing a low angle boundary (marked with arrows). On the left of the photomicrograph the intersections of the four sets of lamellar twins with the flat surface of the specimen deviate from a straight line trace at the boundary due to the angular misorientation of the lattice caused by the boundary.

section of the twins is caused to deviate by the low angle boundary which crosses it. The angular misorientation between the single crystal grains is thus evident. The formation of twins can be understood in principle [27]. A mis-nucleation event on the growth surface that produces a change in the lattice orientation relative to the original growth surface will produce a new region of growth that meets the region of growth corresponding to normal nucleation on at least two surfaces. A crystallographically favourable situation for the surfaces to mate is a twin plane of the type $\{111\}$. The composition plane of the boundary would then be coherent.

Dislocations. — Dislocations were revealed using the previously-noted grain boundary etchant [26]. The etch pit densities were moderately high, but naturally variable. This is understandable since there was evidence of polygonisation. Typical densities were of the order of 1.4×10^5 per cm^2 .

Precipitates. — Precipitates have been observed in slices of crystals when viewed by IR-transmission microscopy. Precipitates appear to be a feature of LEC-CdTe grown from substantially stoichiometric melts. The precipitates occur mainly in grain boundaries although they are by no means confined to them. It has also been noted that regions between certain intersections of some grain boundaries were apparently free of precipitates; this has been noted in other crystals [28]. The precipitates appear as individual elongated opaque particles which when brought into focus at high magnification do not have any obvious crystalline structure. They are about $\sim 1 \mu\text{m}$ in diameter and are typically present in grain boundary sections at a volume concentration of $\sim 5 \times 10^7$ per cm^3 . Figure 6 shows typical precipitates within, and close to, a grain boundary. Figure 7 shows an SEM photomicrograph of precipitates in a section of a grain boundary marked AB and BC. It is evident from the micrograph that only part AB of the grain boundary has any precipitates. The feature X in figure 7 is $\sim 1 \mu\text{m}$ in diameter. A 10 % higher count rate for Te was found in precipitate X when compared with the bulk CdTe. Equivalent results have been found in another crystal. No evidence of this type of precipitate has been detected using IR-transmission microscopy in non-LEC CdTe grown from either excess Cd solution by solvent evaporation or from excess Te solution by the THM method.

Preliminary studies have also been made on LEC crystals grown from melts containing excess Cd or Te. Precipitates were observed in 1 at % excess Cd crystals (2 examined) but not in the 2 at % Cd excess crystals (3 examined). Crystals grown using 1 and 2 at % excess Te (1 crystal of each examined) appeared to show a marked reduction in the precipitate concentration but there was no obvious change in the grain structure. The precipitate results are consistent with Strauss's

FIG. 6. — IR transmission photomicrograph showing precipitates concentrated along a grain boundary. Dispersed precipitates can also be seen at different heights ie in and out of focus.

FIG. 7. — Scanning electron microscope photomicrograph showing a grain boundary ABC. Ignore the large scratch artefact above A. Note the precipitates along AB but not BC. Precipitate X showed a 10 % higher than average Te count when analysed using X ray emission.

suggestion [1] at the last CdTe symposium that the solid phase field lies on the Te-rich side of the phase diagram not on the Cd-rich side, but the results do not constitute a proof of this suggestion.

Discussion. — The presence of low angle grain boundaries has not to our knowledge been noted as a characteristic difference between melt-grown CdTe (and other II-VI's) and the III-V's. The grain boundaries in InSb for example have been systematically investigated by Haasen [29] and almost all the boundaries in a crystal have been shown to be coherent; the lattice orientation between adjacent single crystal

grains bore a characteristic twin relationship. Low angle grain boundaries have not to our knowledge been reported in undoped InSb or in the undoped III-V's. Since their presence in CdTe crystals is a real hindrance to progress it is important to question their origin. They are a feature of metallic crystals but we can find no explanation for their origin from metallurgy.

We frankly do not know the origin of low angle grain boundaries but would suggest the following speculative model based on a comparison between GaAs and CdTe. Both compounds have similar lattice structures, bonding energies and melting points. Diffusion in CdTe however is orders of magnitude greater than in GaAs. CdTe would appear to have a higher point defect concentration (involving vacancies) than GaAs at comparable temperatures. Low angle dislocation boundaries are common in undoped CdTe but not in undoped GaAs. But the density of dislocations found in CdTe cannot explain the low angle grain boundaries. The dislocation densities could only account for misorientations of seconds of arc.

However, the presence of impurities and precipitates in grain boundaries does suggest the possibility that the impurities and vacancies are connected. Vacancy impurity complexes could, it is postulated, have high enough mobilities and be present in sufficient concentration to propagate low angle grain boundaries. Vacancy impurity complexes would probably migrate in the direction of the applied temperature gradient. The significance of interface shape could then be crucial. A concave growth front would have a temperature distribution which would tend to cause vacancy impurity complexes to concentrate towards the centre of the crystal where they could feed and perhaps even initiate low angle boundaries. A convex growth surface could be helpful in avoiding low angle grain boundaries since this would tend to prevent the complexes concentrating and tend to disperse them to the edge of the crystal. Growth at low temperatures by epitaxy or from solution could also be helpful.

6.2 IMPURITIES. — The scope for achieving additional purification by pulling is strictly limited since the crystallization process involves only a single normal

freeze. Indeed, to stand any chance of pulling pure CdTe one requires high purity starting material. The crucial question with melt-growth is whether one can avoid contaminating the original starting material.

The starting materials for the LEC growth of CdTe were as noted previously the elements themselves. Both the Cd and Te were subjected to two zone refining operations (*), the middle section from the first zone refining being used for the second zone refining operation. The B_2O_3 was a grade (**) purified by recrystallisation.

The pulled crystals were analysed by mass spectrometric analysis using an AEI MS702R instrument. Unfortunately Cu and some of the transition elements have limited sensitivity because of interference from isotopes of the matrix elements. In the event however the more serious problem arises from B and Br contamination. Typical analyses of CdTe grown from substantially stoichiometric melts are shown in table II. The Br contamination was traced to the Br_2-CH_3OH etch which was used to clean up the preformed CdTe charge after it had been extracted from contact with B_2O_3 . Minute fissures and cracks in the CdTe charge are a trap for etchant which is difficult to wash clear. This problem is nevertheless potentially soluble.

The B contamination was expected. Boron is a potential donor in CdTe, hence the ability to control the B concentration in LEC crystals may be desirable depending on the use or device application envisaged for the material. The addition of oxides (eg CdO) to the B_2O_3 is a potential way of reducing B contamination. This and other methods have not yet been investigated.

6.3 ELECTRICAL CHARACTERIZATION. — The Hall effect and conductivity of specimens cut from LEC-crystals were measured using the van der Pauw technique. Ohmic contacts to the n-type material were straightforward. They were achieved by alloying in In dots at around 170 °C. Contacts to high resistivity

(*) MCP (Electronics) Ltd., Alperton Wembley Middlesex.
(**) BDH Chemicals Ltd., Poole, Dorset.

TABLE II

Chemical analysis () of LEC-CdTe in ppma*

Element crystal No	B	Br	Zn	As	Al	Ag	Ba	K
CT O16/28	11	12	0.3	< 0.06	0.08	< 0.06	0.05	0.2
CT O37/65	4	2.3	0.15	0.1	< 0.08	0.05	0.04	0.045
CT O40/14	15	4.3	0.15	0.1	≤ 0.3	< 0.05	0.055	0.015
CT O40/36	5	2.6	0.15	0.1	< 0.08	< 0.015	0.025	0.009

(*) Most elements < 0.025 except Ta, $I < 0.8$; S, Si, Mg < 0.25; Sn, Na, Mo < 0.1; Mn, Fe, Ni, Cu, matrix interference, C, O, N not determined.

TABLE III

Some typical electrical/chemical characteristics of LEC-CdTe crystals

Crystal N°	Electrical properties				Chemical properties	
	Carriers per cm ³		Resistivity Ω cm	Mobility cm ² V ⁻¹ s ⁻¹	Major impurities Atoms per cm ⁻³	
	295 K	77 K (**)	295 K	295 K	77 K	
CT O16/25	4.3×10^{17}	4.1×10^{17}	2.2×10^{-2}	646	597	3.2×10^{17} (B) 3.5×10^{17} (Br)
CT O37/65	3.5×10^{17}	—	5.9×10^{-1}	83	—	1.2×10^{17} (B) 6.6×10^{16} (Br)
CT O40/36	3.1×10^{17}	2.5×10^{17}	8.2×10^{-2}	248	731	1.4×10^{17} (B) 7.5×10^{16} (Br)
CT 103	1.5×10^{16}	—	4.3×10^{-1}	922	—	
CT 104	2.2×10^{16}	—	2.9×10^{-1}	965	—	
CT 122 (*)	7.4×10^{15}	—	—	584	—	

(*) 1 at % excess Te added to CdTe melt.

(**) all n-type.

p-type CdTe were not so reliable. The most useful technique following literature practice [6] has been to plate Au on the surface and then contact the Au with In.

The results for typical specimens are reproduced in table III. The carrier concentrations found in crystals grown from substantially stoichiometric melts were around the 10^{16} - 10^{17} carriers per cm³ level. These extrinsic carrier concentrations correlate with the impurity concentrations determined by MS7 analysis within the accuracy of the chemical analyses. Mass Spectrometric analysis is usually reliable to a factor of ± 3 , although experience has shown the results for well behaved elements may well be more accurate. It is interesting that the B and Br₂ concentrations are virtually the same in each crystal. Hence, within the limits of experimental error, either B or Br₂ or the sum effect of both elements could account for the free electron concentration in the crystals. The 77 K mobilities for all the specimens, even those with the fewest apparent free carriers, are lower than the best previously quoted [30] results for uncompensated CdTe.

The results of measurements on crystals grown from melts containing significant amounts of excess Cd or excess Te were not clear cut. The crystals certainly had different properties to those grown from near stoichiometric melts. Further, it was generally found difficult to prepare specimens with van der Pauw contacts which were all truly ohmic when tested at high current densities and low temperatures. Considerable effort was expended in endeavouring to get reliable results on different specimens from different crystals. Most of the specimens appeared to be p-type and of moderate resistivity but until the material is more fully characterised metallurgically the cause of the measurement difficulties cannot be established. Similar problems were encountered with the Te-excess crystals, with the exception of the crystal grown with 1 % excess Te. This had properties similar to the crystals grown from stoichiometric melts.

6.4 PHOTOLUMINESCENCE CHARACTERIZATION. — The photoluminescence spectra of CdTe have not yet been adequately calibrated as a means for identifying che-

mical impurities and impurity complexes in CdTe. In the case of GaAs a systematic study [31] has characterised the common elements which can behave as acceptors in the crystal. But, for identification purposes it is necessary that the GaAs be sufficiently pure, less than $\sim 10^{16}$ carriers per cm³ for p-type material and less than $\sim 10^{15}$ carriers per cm³ for n-type material, and further the GaAs should be of good crystal perfection. In situations where the crystals are less pure and less perfect the photoluminescence spectrum can serve as a useful guide to the quality of the material. In the following section therefore some results are discussed on the photoluminescence spectra of LEC-CdTe and some observations are made on how these spectra compare with spectra recorded from CdTe prepared by other growth techniques.

The basic features of the photoluminescence spectrum of CdTe can be appreciated from a simplified materials viewpoint by considering three principal regions. There are exciton lines within about 20 meV of the band edge. There are various lines in the region ~ 1.53 - 1.55 eV some of which are attributed to donor/acceptor transitions involving the cadmium vacancy and there is an emission band around 1.40 eV with strong classical phonon replicas showing a Poisson distribution in energy.

The first notable characteristic of LEC crystals is that they do not show sharp exciton lines. Structure in the exciton spectra is normally only a feature of purest crystals possessing the best physical quality. Material grown at low temperatures from Te solution has revealed the best exciton spectra we have seen so far.

The most impure crystals, those with free electron concentrations around 3×10^{17} electrons per cm³, emitted a broad luminescence band around 1.4 eV showing little or no significant structure. An example of the luminescence spectra from a purer good average crystal is shown in figure 8. At 5 K one can see near the band edge the donor exciton line at 1.5913 eV together with the acceptor exciton line at 1.5884 eV line [32, 33]. The lines labelled A_0 , B_0 and C_0 together with phonon replicas at $E_x - (nx 0.021)$ eV are believed to be due to acceptors. They are pair bands associated with D/A

FIG. 8. — Photoluminescence spectra taken from an LEC crystal showing the effect of increase of temperature. A_0 , B_0 and C_0 are believed to be pair bands due to acceptors. Their phonon replicas at $E_x - n \cdot 0.021$ eV can also be seen. Increasing the temperature from 5 K to 10 K and 15 K progressively reveals the FB transitions associated with the pair bands.

pairs. The corresponding free-to-bound peaks can be progressively revealed by taking spectra at higher temperatures as shown in figure 8. These lines are not new, the consensus view of the A_0 pair line being that it is associated with the Cd vacancy.

The C_0 line and its associated replicas constitute the 1.4 eV emission band mentioned earlier. The intensity of this band is sensitive to the conditions of crystal growth. The band is virtually absent in crystals prepared by evaporation of cadmium from cadmium-rich melts. Agrinskaya *et al.* [34] consider that the band is connected with the formation of V_{Cd} -donor complexes. The present results do not conflict with this viewpoint. Certainly the C_0 band is strong in CdTe grown from Te-rich solutions. A more detailed analysis of these spectra will be reported elsewhere.

7. Conclusions. — At the present stage of development the LEC technique can be used for growing crystals with at best large single crystal grains say 10 mm × 5 mm × 50 mm. The major hindrance to the growth of large single crystals would appear to involve understanding and controlling the formation of low angle grain boundaries and twins. Like other melt-growth techniques it does not produce the purest crystals, which in the semiconductor field are now

achieved by growth at lower temperatures. Provided B contamination is not a problem or can be controlled the LEC technique does offer scope for the ready production of doped material for various studies.

In cases where crystals need to be prepared in a controlled Cd or Te atmosphere a pulling technology involving Pressure Balancing is suggested as a method with potential merit.

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