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CRYSTAL GROWTH BY SOLVENT TECHNIQUES AND CHARACTERISTIC PROPERTIES OF CdTe

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Résumé. — On a déterminé les conditions optimales de croissance de monocristaux de tellure de cadmium non dopés à partir d'une solution riche en tellure par la méthode THM. Dans nos conditions expérimentales, il apparaît qu'une température de croissance de 650 °C et une vitesse de 3 mm par jour constituent le meilleur choix. Dans ces conditions, les cristaux de type p présentent une résistivité de $10^6 \Omega \cdot \text{cm}$. Lorsqu'une suppression de cadmium règne au-dessus de la solution de tirage, la résistivité peut même atteindre $8 \times 10^6 \Omega \cdot \text{cm}$. Pour une pression de cadmium convenable des cristaux de bonne qualité peuvent être obtenus dans lesquels les porteurs ont des longueurs de diffusion importantes. D'autres études de caractérisation de ces matériaux sont présentées utilisant les propriétés de transport des porteurs ou des mesures de photoluminescence.

Abstract. — Optimum growth conditions to grow pure single crystals from Te-rich solution by the Traveling Heater Method are investigated. For the growing apparatus employed, the optimum conditions are determined to be a growth temperature of 650 °C and a growth rate of 3 mm/day. The room temperature resistivity which we obtain in undoped p-type crystals extends to nearly $10^6 \Omega \cdot \text{cm}$. When the Cd pressure over the Te solution is controlled during crystal growth, the room temperature resistivity can be increased to $8 \times 10^6 \Omega \cdot \text{cm}$. Characterization of the crystals grown by the Traveling Heater Method is also carried out by means of carrier transport and photoluminescence measurements, and it can be shown that under an appropriate Cd pressure, excellent crystals with good transport properties for both electrons and holes are obtained.

1. Introduction. — CdTe is a very promising material for the fabrication of γ -ray spectrometers operating at room temperature because of its large mean atomic number coupled with a sufficiently high bandgap and reasonable mobilities for both carriers. Thus, the past five years have seen much work devoted to explore its properties for this purpose including crystal growth, radiation detector fabrication and electrical characterization [1-7]. However, to date lack of very high energy resolution is still a drawback in these devices and the lack of performance has generally been attributed to carrier trapping [8-10]. Martin *et al.* [9] have suggested two levels which limit τ_h^+ but they also showed that for the better values of τ_h^+ , which ranged up to 1 500 ns, excellent detector performance can be achieved.

Shallow electron trapping levels at 0.02 and 0.05 eV have also been found [5, 10] but they influence detector performance at room temperature only a little, but a deeper trapping level at $E_c - 0.6$ eV can reduce $\mu\tau_e^+$, [10] and more seriously, levels of such depth have been implicated in causing detector polarization [5, 11]. This latter level is somewhat speculatively assigned to be a doubly ionized cadmium vacancy (V_{Cd}''). Such vacancies are inevitably created during donor doping since CdTe has a strong tendency for self compensation

However, in spite of a great deal of investigation,

the detailed origin of all the traps is still unclear, even though there is general agreement that most of them are due to either native defects, in particular Cd vacancies, or their association with various donor dopants.

But even in undoped material grown from Te solution at low temperature there is still a small deviations from stoichiometry, causing Cd vacancies. If such vacancies then are held responsible in one way or the other, for causing trapping or polarization, any possible reduction in the vacancy content is of course extremely important. The present paper then concerns itself with the question as to whether the vacancy content could be reduced by introducing a Cd overpressure during crystal growth from Te solutions.

2. Crystal growth from Te-rich solution. — Although a variety of methods have been used to grown CdTe for γ -ray detector purposes, we have convinced ourselves that growth from Te-rich solutions, in particular using the *Traveling Heater Method* (THM)[1] is the simplest and most reliable way to obtain the material for the purpose. This is due to the following advantages :

- i) reduced contamination from the crucible ;
- ii) low growth temperatures, which decreases the native defect content ;
- iii) the gettering effects of the solvent metal.

FIG. 1. — a) Electrical properties of THM grown crystals demonstrating p-type behavior dominated by $E_v + 0.15$ eV acceptors. b) Comparison of photoluminescence spectra of Bridgman and THM grown CdTe.

It should be mentioned here that vapor growth, aside from not providing gettering effects, should show similar advantages though, but it has not been widely used yet for the growth of large crystal volumes of CdTe.

We have confirmed the higher purity of Te grown crystals which has been reported before [1, 15] using ion beam microanalysis. Compared with Bridgman crystals, Fe, Al, Si, Cr and Ca, which are the dominant impurities, are all considerably reduced. Furthermore, figure 1 demonstrates the remarkable reduction in the 1.42 eV emission in a photoluminescence spectrum taken at 4.2 K, when Bridgman grown and solution grown material are compared.

However, we have observed that the characteristics of the Te grown material are very dependent on the growth conditions such as growth rate and temperature. Figure 2 shows a schematic representation of our growth setup [13]. The width of the Te zone at the center of the furnace is chosen to be 10 mm. Material grown by the Bridgman method is used as feed in a quartz tube with an inner diameter of typically 10-15 mm. The growth temperature at the central zone (zone 3) and the growth rate are separately varied to obtain optimum growth conditions. Figure 3 shows the relation between the growth temperature and the room temperature electrical properties for undoped material grown at 3 mm/day and 5 mm/day. Both of these rates give essentially the same results. We see that the hole mobility is virtually constant at about $90 cm^2/V \cdot s$ for all temperatures studied, but the hole concentration which could be confirmed to be gover-

FIG. 2. — Schematic representation of CdTe crystal growth from Te-solution by THM.

ned by acceptors at $E_v + 0.15$ eV, increases rather rapidly at growth temperatures over $675^{\circ}C$. A semi-logarithmic plot of hole concentration vs. $1/T$ yields an activation energy of about 3.0 eV, a rather high value which is not readily understood.

The dependence of the electrical properties on the growth rate over a larger range of rates at $675^{\circ}C$ is shown in figure 4. From about 7 mm/day upwards, the results get progressively worse in electrical terms,

FIG. 3. — Effect of growth temperature on the room temperature electrical properties of THM grown material at two constant rates (3 mm/day and 5 mm/day).

FIG. 4. — Effect of growth rate on the room temperature electrical properties of HM grown CdTe at a constant growth temperature of 675 °C.

and on exceeding 14 mm/day, we can only obtain polycrystalline ingots. This is a clear improvement in the growth rate for single crystal ingots over the results reported by Bell *et al.* [1].

From these results, we reach the conclusion that for our particular furnace the conditions for growing crystals with optimum electrical transport properties a rate of 3 mm/day at 650 °C, although some tolerance on these values is probably allowed. Under these conditions we obtain resistivities as high as $10^6 \Omega \cdot \text{cm}$ for our not intentionally doped crystals.

Also, studies of etch pit densities reveal very low values of $5 \times 10^2/\text{cm}^2$ for these conditions and a gradual increase to about $10^3/\text{cm}^2$ as the growth temperature is increased. However, when the rate is increased over 3 mm/day, dramatic increases in etch pit density are observed. No improvements in any of the properties are noted, however, when the rate is decreased below 3 mm/day.

3. Effect of Cd overpressure on THM crystals. —

Although fairly pure crystals can be grown by THM, the p-type conductivity of the resulting CdTe is still governed by the $E_v + 0.15 \text{ eV}$ acceptors which are caused by a complex containing Cd-vacancies. Thus, one is led to the idea that kinetic limitations of Cd-transport of CdTe interface dissolution in non-steady state conditions and lead to excess Cd vacancy introduction, which might explain the various dependencies of the electrical properties on temperature and growth rate which have been described above. Consequently, if one could control the Cd-overpressure over the Te solution, one might be able to reduce the Cd vacancy concentration.

FIG. 5. — Schematic of THM growth of CdTe under controlled Cd-overpressures.

Hence, we modified the THM method to obtain a controlled Cd overpressure as shown in figure 5, which should be studied carefully. As can be seen, we control the temperature of a Cd reservoir between 1 000 °C and 1 140 °C but we believe the Cd pressure in the upper part of the ampoule to be effectively controlled by T_1 , the temperature of the feed region. Temperatures between 300 °C and 560 °C are used for T_1 and the growth temperature is held constant at 700 °C with a rate of 3 mm/day.

The electrical results obtained are plotted in figure 6. Increasing T_1 , the resistivity increases until it reaches a maximum of $8 \times 10^6 \Omega \cdot \text{cm}$ for $T_1 = 480^\circ\text{C}$. When T_1 is raised over 500°C the room temperature resistivity decreases as $P_{\text{Cd}}^{-1/3}$ if we assume the Cd pressure to be indeed determined by the temperature T_1 of the CdTe feed, but p-type conductivity is maintained.

FIG. 6. — Resistivity as a function of feed temperature with two constant Cd reservoir temperatures.

To look at the most extreme condition, we also obtained crystals grown from pure Cd solution in steady state. Such crystals now show n-type conductivity governed by donors at about $E_C - 0.05 \text{ eV}$. Figure 7 shows photoluminescence spectra at 4.2 K and 77 K for crystals grown under various Cd overpressures, where the Cd overpressure again is deduced simply from T_1 . The emission intensity of the 1.42 eV band, however, increases monotonically even beyond the point where the resistivity starts to decrease.

4. Detailed photoluminescence results. — Photoluminescence measurements allow information to be obtained concerning localized levels due to impurities and defects [14].

So far as the 1.42 eV band is concerned (Fig. 1) we can show, that, qualitatively at least, it increases when donor doping increases, which is the case for introduction of Cl, Br, In, Ga, Li, and Cd interstitials. This we ascribe to the fact that all these donors cause increases in the Cd-vacancy concentration due to self compensation effects. And we feel it is confirmed also by the facts presented in figure 7, which show that with increasing Cd-overpressures the 1.42 eV emission intensity increases, even though at the higher pressures the resistivity decreases. This decrease then is ascribed to Cd interstitial formation due to the fact that the resistance has a $P_{\text{Cd}}^{-1/3}$ dependence on Cd overpressure [15]. Finally, however, when crystals are grown from Cd-solution, we find an emission line

FIG. 7. — a) Ratio of the resistivity at a specific Cd overpressure (assumed to depend only on the feed temperature T_1) to the resistivity of CdTe grown from Te solution above. b) Photoluminescence spectrum of CdTe grown under Cd-overpressures.

FIG. 8. — Photoluminescence spectrum of CdTe grown from Cd solution.

at 1.553 eV (Fig. 8) assigned to a donor at $E_C - 0.054 \text{ eV}$ which could result from a Te vacancy complex [16] although this is at present pure speculation.

FIG. 9. — Photoluminescence spectrum of Na — doped CdTe.

However, in accordance with this general model we find that acceptor doping with Au or Na has no influence on the intensity of the 1.42 eV emission or indeed may suppress it. Sodium doped crystals specifically show p-type conductivity caused by shallow acceptors at $E_v + 0.026$ eV. In the photoluminescence spectrum, figure 9, correspondingly, lines at 1.584–1.583 eV are seen which correspond to transitions from the conduction band to acceptors 0.022–0.023 eV above the valence band. In this crystal, furthermore, the 1.42 eV emission band is hardly visible. This suggests to us that Cd vacancies are almost absent here, with Na occupying Cd site, in particular since no changes were made in the growth experiments. The photoluminescence spectra of Na doped crystals, therefore, appear to show a way to reduce Cd vacancy concentration by careful Na doping.

We have also made a number of detailed measurements of photoluminescence on these crystals on which we have reported previously [17]. We had come to the conclusion there, that in p-type THM grown crystals the most dominant line at 1.59 eV (I_a) is due to annihilation of excitons bound to neutral acceptors which we place at 0.06 eV above the valence band. This idea we feel is further supported by measurements which we have now made in which it can be demonstrated that weakening of the I_a line leads to increases in both the intensity of the free exciton line at 1.595 eV and the emission line I'_0 at 1.545 eV which is the line of the acceptor itself. We have also carried out more detailed experiments using the Zeeman effect to elu-

cidate the structure of this acceptor and have come to the conclusion that it is a complex along the [111] direction possessing C_{3v} symmetry [18].

5. Conclusions. — The *Traveling Heater Method* is held to be most useful in growing bulk CdTe single crystals of high purity, since it has been demonstrated here that for crystals grown under optimum thermal and rate conditions, etch pit density, chemical purity, electrical properties and photoluminescence spectra all optimized.

We have also studied the effects of Cd overpressures on the characteristics of the crystals grown. When based on the feed temperature, we can show that a Cd-overpressure of 3×10^{-3} atm. maximizes the room temperature resistivity of undoped p-type crystals grown from Te solution. It can be as high as $8 \times 10^6 \Omega \cdot \text{cm}$. However, crystals of the highest resistivity are not necessarily best in terms of electrical transport properties. In fact, these are maximized at over pressures around 10^{-3} atm, as will be explored in more detail in our other paper, also presented at this symposium.

However, our attempt to totally suppress Cd vacancies by Cd-overpressures was not successful, although improvements were achievable. We ascribe this at present to the self compensation tendencies of CdTe.

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