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Comparison of Two Approaches to Forced Convection in Crystal Growth of II-VI Compounds by THM

R. U. Bloedner, M. Presia* and P. Gille

Institut für Kristallographie und Materialforschung, Fachbereich Physik, Humboldt-Universität zu Berlin, Invalidenstr. 110, 10115 Berlin, Germany

Hg_{1-x}Cd_xTe and Cd_{1-x}Zn_xTe single crystals were grown by the travelling heater method (THM), applying two different techniques of artificially stirring the solution zone. Accelerated crucible rotation (ACRT) was used in a vertical growth arrangement and compared a technique with constant rotation around the horizontal axis of the ampoule. The dominant hydrodynamic mechanisms of both methods are described by the rotating disc model and are suggested to be almost identical with respect to the growth conditions at the interface. Convective flow is effectively enhanced adjacent to the growing crystal, where the matter transport is regarded as the rate-limiting step of solution growth. Inclusion density analysis by IR microscopy was used to characterise the crystals of Cd_{1-x}Zn_xTe grown at different rates. It was shown that forced convection allows an increase in the crystal growth rate from a few mm day⁻¹, typical of natural convection regimes, to more than 10 mm day⁻¹ with ACRT or horizontally rotating THM.

KEYWORDS Solution growth THM HgCdTe CdZnTe Forced convection ACRT
Solvent inclusions IR microscopy

INTRODUCTION

Whereas for centuries it had been believed that no stirring should be the best condition for a growing crystal, it was about 100 years ago when external and internal stirring of aqueous solutions during crystal growth was used for the first time. For about two decades forced convection applied to crystal growth has been intensively studied. In 1972 Schulz-DuBois¹ gave the theoretical description of a new technique of stirring a liquid and its effect on material transport in crystal growth. This has been proved to be a valuable tool in making the crystal grower familiar with the relevant hydrodynamic mechanisms. It was Scheel² who first applied this technique, called accelerated crucible rotation technique (ACRT), to crystal

growth from high-temperature solutions. In his study, ACRT allowed faster solution flow rates resulting in inclusion-free crystals, even with increased growth rates. The same has been found comparing CdTe crystals grown by THM from Te-rich solution zones under ACRT and non-ACRT conditions³.

In Bridgman growth of Hg_{1-x}Cd_xTe, ACRT has been primarily used not to increase the rate, which is much higher than in solution growth methods, but to influence the segregation behaviour by forced convection. Without ACRT, Bridgman growth of Hg_{1-x}Cd_xTe suffers from the problems of the high segregation coefficient and a strong composition dependence of the mass density. These material properties result in either axial or radial inhomogeneity of the crystals, depending on whether the growth rate was low or high^{4,5}. The application of ACRT to the

Present address: Institut für Werkstoffe, Technische Universität Ilmenau, PF 327, O-6300 Ilmenau, Germany.

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Bridgman growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ has proved to effectively influence the solid-liquid interface shape⁶ and to improve both, radial and axial compositional uniformity^{7,8}.

Forced convection in THM is not aimed at the improvement of x -distribution which has been shown to be sufficiently homogeneous to meet the high requirements of device fabrication⁹⁻¹². The main problem with THM is the typically low growth rate of a few mm day^{-1} , which is limited for material transport reasons. Therefore, we have investigated forced convection in THM growth of II-VI alloys to increase the rate without degrading structural perfection and compositional uniformity of the crystals. $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ is regarded as the preferred material for practical use of THM, whereas within this study, $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ primarily serves as a model substance, being transparent in the spectral range used for inclusion investigation.

is thrown outward due to centrifugal forces acting upon it. This outward flow is balanced for reasons of continuity by a flow in axial direction towards the disc to be in turn carried and ejected centrifugally. In the vicinity of the rotating disc the axial flow velocity amounts to

$$v \propto \omega^{3/2} \nu^{-1/2} \quad 1$$

with ω being the rotation rate and ν the kinematic viscosity. Thus, the axial flow turns out to be independent of the radial position.

The two arrangements used to realise the model of the rotating disc in practical THM growth processes are shown in Figs 1 and 2. In the vertical arrangement, which is typical of other THM studies published so far, a permanent motion between the solid and liquid phases can only be generated by accelerated crucible rotation¹³.

BASIC IDEAS

As it has been shown in detail in a recent paper¹³, the maximum stable growth rate in THM can be increased by the expansion towards the interfaces of that region which is stirred by convection. Rotation of the solid interface relative to the liquid phase is widely accepted to be one way to achieve this. Such a motion produces convection flows which are approximately equivalent to those arising from the rotation of an infinite disc in a viscous liquid staying at rest.

Von Kármán, who gave a mathematical description and a solution of the latter problem¹⁴, showed that the layer of the liquid adjacent to the rotating disc is carried by it through friction and

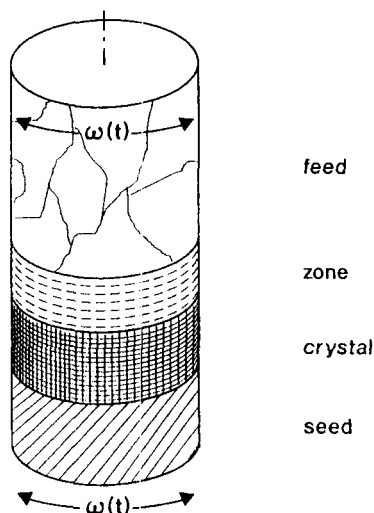


Fig. 1. Schematic representation of the THM crystal growth arrangement used in the vertical ACRT experiments

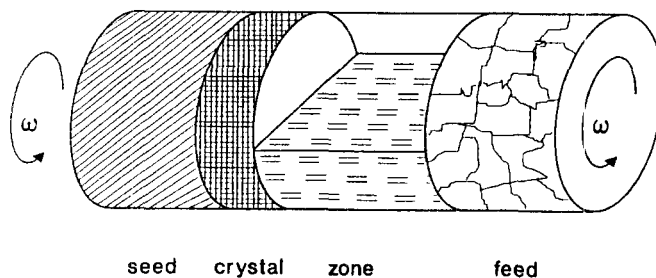


Fig. 2. Schematic representation of the horizontally rotating THM arrangement

Because of the fact that there has been some discussion in the literature, whether the oscillatory nature of ACRT should cause the growing crystal to record the periodicity of the growth conditions, a more continuous growth regime should be preferred. That is, why in a second set of experiments we have investigated a modified THM arrangement with a crucible homogeneously rotating ampoule around its horizontal cylinder axis¹⁵ (see Fig. 2).

Both approaches have almost the same influence on the convection flows in the liquid zone whereas the differences lie in the continuity of the slip motion with the horizontal method and in the different cross sections of the zone.

EXPERIMENTAL

Both, ACRT and horizontal THM experiments were carried out in evacuated, closed silica ampoules that had been graphite-coated beforehand. Seed crystals being $\langle 111 \rangle$ or $\langle \bar{1}\bar{1}\bar{1} \rangle$ orientated were prepared from Bridgman-grown CdTe or (Cd,Zn)Te single crystals. Seed and feed ingots were carefully ground as to perfectly suit the inner diameter of the ampoule. $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x \approx 0.1$) feeds were quenched from stoichiometric melts, whereas $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($0.2 \leq x \leq 0.3$) source ingots were prepared by a first THM pass which has been described in a previous paper¹¹. Use was made of unsaturated tellurium zones. In both sets of experiments, crystals were grown in simple one-zone resistance heaters creating axial temperature gradients of about 100 K cm^{-1} in the liquid adjacent to the phase boundaries. Ampoule rotation was adjusted with a goniometer head. For $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ the growth temperature was about 750°C , whereas for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ the temperature was chosen as about 500°C because of its much higher solubility. Tellurium zones were always calculated as to yield a length after saturation that approximately equals the diameter of the ingot (16 mm).

ACRT Experiments

For the vertical experiments the ACRT cycle was not varied. The spin-up/spin-down time was calculated using the related equation given by Schulz-DuBois¹ and the geometric and hydro-

dynamic parameters of the materials used in the present study. Because of a lack of exact data, the dynamic viscosity was taken for pure tellurium³. In order to enhance axial flow, high rotation rates are desirable (see Eq. 1). However, apart from unstable Ekman flow occurring at too high an acceleration, the maximum rotation rate was limited by the mechanical stability of the growth equipment to $\Omega_0 = 200 \text{ rev min}^{-1}$, resulting in an acceleration/deceleration of about $d\omega/dt = \pm 0.9 \text{ s}^{-2}$. Reverse of rotation was carried out without intentional rest. In order to relate the growth rates to the individual axial crystal segments, the translation rate was increased step-by-step after every constant length grown under fixed conditions.

Horizontal Rotation Experiments

The two parameters fixing the length and height of the solution zone in a given temperature profile are the amount of pure solvent and the distance between seed and feed. Thus, zone preparation is the most important starting condition. This was done by cutting a segment out of a cylindrical Te piece or by casting a wedge-shaped starting zone. A constant rotation rate of $\omega = 100 \text{ rev min}^{-1}$ was used, which is thought to be comparable to the average relative motion between solid and liquid in ACRT. The growth rate was varied in the same way as in the ACRT experiments. Growth was finished by slow cooling or sometimes by quenching to fix both the zone position and interface shape.

RESULTS AND DISCUSSION

General Features

Both techniques of stirring the solution zone in THM experiments have proved to make single-crystal growth possible^{13,15}. While crystals grown with ACRT look like the usual result of a THM growth run, the horizontally grown crystals reveal their special growth conditions when the process has been finished by simultaneously quenching the zone and stopping the ampoule rotation (see Fig. 3). As can be assumed from simple hydrodynamic considerations, with enhanced radial flow next to the crystalline interfaces their shape should be influenced not only by the curvature of

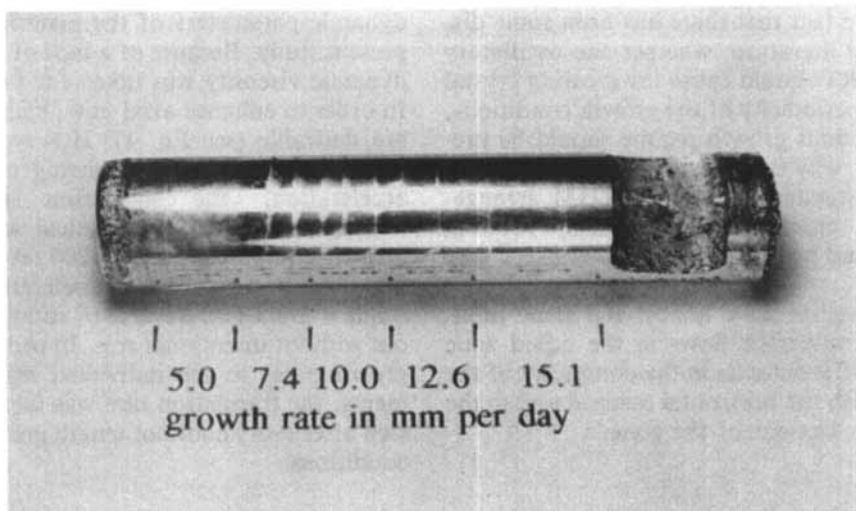


Fig. 3. Photograph of a crystal grown by THM with horizontal ampoule rotation. The liquid zone has been quenched to fix its position (crystal diameter 16 mm)

the relevant isotherms but also by the hydrodynamic regime. There is only some evidence that in horizontally rotating experiments the crystals grow with a slightly concave interface shape, whereas a flat or slightly convex one should result from the thermal field alone. This dependence needs further experiments using a wider variation in the rotation rate.

The metallurgical properties of the grown alloys, especially $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, show no principal difference in the macroscopic distribution behaviour compared to crystals grown under natural convection conditions. As expected, this is true for both axial as well as radial uniformity. A typical plot of the x distribution of an $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystal grown in an ACRT regime is

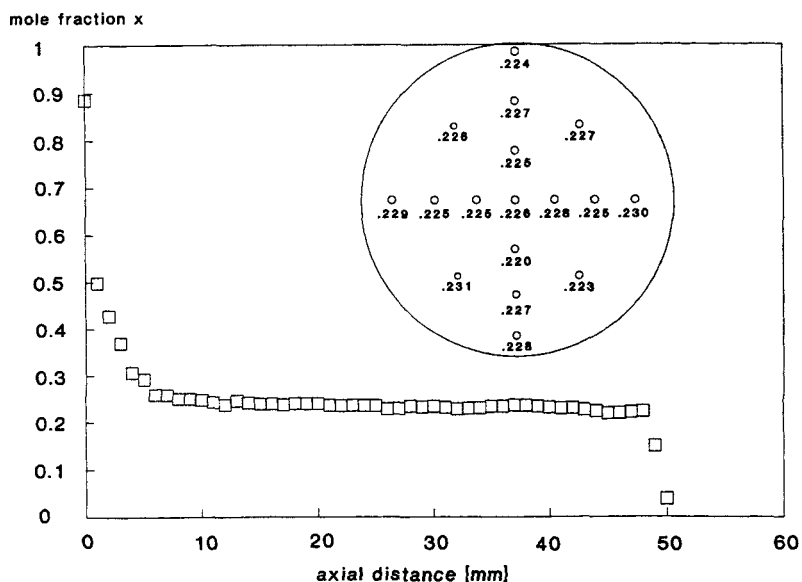


Fig. 4. Axial mole fraction profile and radial plot of an $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystal grown in an ACRT regime (electron probe microanalysis measurements using $\text{Cd } L_{\alpha}$ radiation, crystal diameter 16 mm)

shown in Fig. 4. With horizontal THM growth the transient decrease in the axial x profile is steeper due to the smaller total amount of solution in the half-zone configuration.

Influence of the Growth Rate

As described before, the analysis of mother liquid inclusions in the grown crystals should indicate the maximum possible growth rate. Infrared microscopy was used to investigate the distribution of tellurium inclusions in 1 mm thick $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ slices cut perpendicular to the growth direction. Inclusion analysis has not been done with $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, because the low- x material is opaque in the range of infrared light up to several micrometres and only those inclusions that accidentally intersect the surface of the slice can be detected by optical microscopy.

Generally, there are two different types of tellurium inclusions. Large inclusions with mean diameters of about $50\ \mu\text{m}$ are the characteristic defects located on the periphery of the slices up to a distance of 1 mm from the edge. The largest of them have a regular shape corresponding to the matrix orientation. If grain boundaries exist, the same type of inclusions are frequently present and decorate the boundaries. These two phenomena are not just typical of THM crystals grown under forced convection conditions, but also occur in crystals grown in a non-ACRT regime. Consequently, we have found them to be almost independent of the growth rate applied. Regarding the much lower flow rates in the blind angles next to the ampoule wall or at the intersection of a phase boundary and the growing interface, the large number and size of these inclusions can be explained. This type is not so important, since grain boundaries can be avoided and the periphery of a crystalline ingot is removed prior to any kind of application.

The second type of solvent inclusion, which is typically of the order of about $5\ \mu\text{m}$ in diameter, is more interesting. These inclusions are almost homogeneously distributed and do not lie on grain boundaries or other particular locations. Crystals grown in the ACRT regime have an inclusion density of about $5 \times 10^4\ \text{cm}^{-3}$, which is a relatively low one for solution-grown crystals. While raising the growth rate up to $12.3\ \text{mm day}^{-1}$, we have not found any increase in the inclusion density (see Fig. 5(a)). Growth rates higher than $12.3\ \text{mm day}^{-1}$ have not been applied

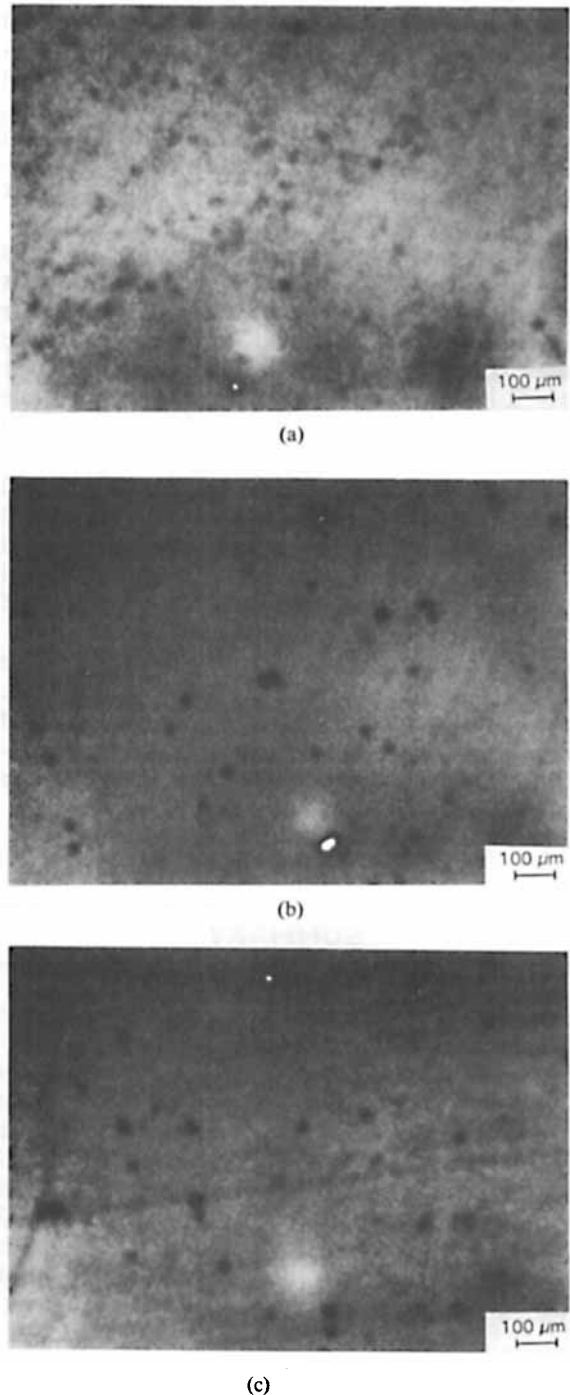


Fig. 5. Tellurium inclusions in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ slices ($800\ \mu\text{m}$ thick) investigated by infrared microscopy ($\lambda = 1.1\ \mu\text{m}$) grown with (a) ACRT-assisted THM at a growth rate of $12.3\ \text{mm day}^{-1}$, (b) horizontal crucible rotation at a growth rate of $7.6\ \text{mm day}^{-1}$ and (c) horizontal crucible rotation at a growth rate of $15.1\ \text{mm day}^{-1}$.

in the ACRT experiments, to date. Referring to all the analysed properties of the crystals grown by ACRT-assisted THM up to this limit, the growth rate has no influence on the crystal.

Smaller inclusion densities (less than $2 \times 10^4 \text{ cm}^{-3}$) have been found with the horizontally grown crystals of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ up to a rate of 7.6 mm day^{-1} , which can be seen from Fig. 5(b). Increasing the growth rate to 10.0 mm day^{-1} , no increase in density was observed. Only for rates higher than 12.6 mm day^{-1} the growth rate slightly influence the inclusion density. Growth with the highest rate used (15.1 mm day^{-1} , see Fig. 5(c)) produced a density of small-scale inclusions of about $5 \times 10^4 \text{ cm}^{-3}$ in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals.

The different densities of mother liquid inclusions of the two approaches may be caused by the differences in the growth temperature used which was much higher in the case of horizontal rotation (about 800°C) than in the case of ACRT-assisted THM (about 720°C).

On the basis of the theoretical arguments above and the results obtained by ACRT-assisted THM, the behaviour of tellurium inclusions in THM crystals grown under forced convection conditions should be further investigated with higher growth rates than used so far.

SUMMARY

ACRT and horizontal rotation around the ampoule axis have proved to be effective techniques to enhance convective flow within Te-rich solution zones in THM growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. Forced convection close to the growing interface markedly increases the crystal growth rate. Rates as high as 12 mm day^{-1} with ACRT and 15 mm day^{-1} with the horizontal rotation technique were applied to THM growth without substantially degrading the structural perfection.

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REFERENCES

1. E. O. Schulz-DuBois, *J. Cryst. Growth*, 1972, **12**, 81–87.
2. H. J. Scheel, *J. Cryst. Growth*, 1972, **13/14**, 560–565.
3. F. V. Wald and R. O. Bell, *J. Cryst. Growth*, 1975, **30**, 29–36.
4. B. E. Bartlett, P. Capper, J. E. Harris and M. J. T. Quelch, *J. Cryst. Growth*, 1979, **46**, 623–629; **47**, 341–350.
5. P. Capper, J. J. G. Gosney, C. L. Jones and M. J. T. Quelch, *J. Cryst. Growth*, 1983, **63**, 154–164.
6. P. Capper, W. G. Coates, C. L. Jones, J. J. Gosney, C. K. Ard and I. Kenworthy, *J. Cryst. Growth*, 1987, **83**, 69–76.
7. P. Capper, J. J. Gosney and C. L. Jones, *J. Cryst. Growth*, 1984, **70**, 356–364.
8. P. Capper, J. J. Gosney, C. L. Jones and E. J. Pearce, *J. Electron. Mater.*, 1986, **15**, 361–370.
9. R. Triboulet, T. Nguyen Duy and A. Durand, *J. Vac. Sci. Technol. A*, 1985, **3**, 95–99.
10. B. Baird, P.-K. Liao, R. Chang and L. Colombo, *J. Cryst. Growth*, 1989, **98**, 595–609.
11. P. Gille, F. M. Kiessling and M. Burkert, *J. Cryst. Growth*, 1991, **114**, 77–86.
12. C. Genzel, P. Gille, I. Hähnert, F. M. Kiessling and P. Rudolph, *J. Cryst. Growth*, 1990, **101**, 232–236.
13. R. U. Bloedner and P. Gille, *J. Cryst. Growth*, 1993, **130**, 181–187.
14. Th. von Kármán, *Z. Angew. Math. Mech.*, 1921, **1**, 233–252.
15. P. Gille, M. Presia, R. U. Bloedner and N. Puhlmann, *J. Cryst. Growth*, 1993, **130**, 188–194.