EFFECTS OF CRYSTAL GROWTH PROCESS PARAMETERS ON THE
MICROSTRUCTURAL OPTICAL AND ELECTRICAL PROPERTIES OF
CdTe AND CdMnTe

by

JAMES SPIROS NAKOS

B.S., University of Massachusetts, Amherst (1977)

Submitted to the
Department of Materials Science and Engineering
in partial fulfillment of the requirements for the degree of

DOCTOR of PHILOSOPHY

at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

MAY 1988

(C) Massachusetts Institute of Technology

Signature of author  ________________________________
Department of Materials Science and Engineering
April 29, 1988

Certified by ________________________________
August F. Witt
Thesis Supervisor

Accepted by ________________________________
John B. VanderSande
Chairman, Departmental Committee on Graduate Students

JUN 6 1988

LIBRARIES
ARCHIVES
EFFECTS OF CRYSTAL GROWTH PROCESS PARAMETERS ON THE MICROSTRUCTURAL
OPTICAL AND ELECTRICAL PROPERTIES OF CdTe AND CdMnTe

by
James Spiros Nakos

Submitted to the Department of Materials Science and Engineering on April 29, 1988 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The relationships between crystal growth process parameters and the microstructural, optical and electrical properties of CdTe and CdMnTe are examined. In particular the influence of the lowering rate, interface location, interfacial thermal gradient (axial), seed orientation, ampule design, stoichiometric deviation, and ampule rotation are explored.

A computer controlled vertical Bridgman/Stockbarger furnace system was designed and constructed which provides improved heat transfer control during growth. The system incorporates an extension of the dual heatpipes separated by an insulating zone design. A nickel heat leveler combined with a specially designed heater element was developed, which permits growth of materials at temperatures exceeding the maximum operating limit of present day heatpipe technology. Quasi steady state growth has been achieved using the system. The initial interface shape is found to be flat within 0.5 mm, the resolution of the measuring technique.

For a constant reservoir temperature, infrared microscopy indicates an increase in precipitate density accompanies increased growth rates, from 0.2 cm/hr to 1.2 cm/hr. Virtually precipitate free growth is observed for a growth rate of 0.2 cm/hr. At rates of 1.2 cm/hr inclusions are observed near the crystal periphery. Increased growth rates also result in an increased tendency to produce polycrystalline material. The effect is consistent with constitutional supercooling.

Relocating the initial melt-solid interface from near the hot zone to near the cooler zone does not appear to have any strong influence on the growth behavior. Heat transfer analysis of the system suggests that only a 3% change in interface deflection is attained by this procedure. The modeled behavior suggests that modifications of the interface shape are limited by presence of the ampule. Results obtained utilizing increased axial gradients, from ~20°C/cm to ~40°C/cm, suggest that improved grain selection is possible. Heat transfer analysis indicates that a 15% change in interface deflection can be achieved in this configuration.
Reproducible seeding of CdTe in a vertical Bridgman/Stockbarger configuration was achieved. The initial melt solid interface position could be predicted to within ±2.0 mm using an analytical heat transfer model and was reproducible to better than ±1.0 mm. Seeded growth in the ⟨100⟩, ⟨110⟩, ⟨111⟩ directions suggests that ⟨110⟩ growth is preferred. Seeding in the ⟨100⟩ directions initiated immediate polycrystalline growth. Studies utilizing a variety of growth configurations also suggest that ⟨110⟩ growth is preferred, but is a subset of growth in any direction perpendicular to ⟨111⟩. Propagation of twin lamellae parallel to the growth axis for distances of over 10 cm is observed for ⟨110⟩ growth. Twins are shown to be capable of 'sinking' dislocations forming composite structures which can act as sites of precipitate nucleation. Sections of increasing crystal (ampule) diameter are identified as sites initiating polycrystalline growth.

Control of the component vapor pressure over the melt has been achieved by incorporation of an isothermal reservoir zone. For growth at constant lowering rate, the density of spherical precipitates observed by infrared microscopy is found to increase as the reservoir temperature decreases to below 750°C. Scanning transmission electron microscopy indicates the precipitates observed are composed of tellurium. Virtually no spherical precipitates are observed for reservoir temperatures above 750°C. Hall effect measurements indicate p-type behavior with carrier concentrations of between $5 \times 10^{13}/\text{cm}^3$ to $1 \times 10^{14}/\text{cm}^3$ independent of reservoir temperature. A similar lack of dependence of the absorption coefficient is consistent with precipitation of native defects. Resistivity vs temperature measurements reveal a trap level at 0.147 ± 0.020 eV which apparently dominates the electrical properties. Growth from a cadmium rich liquidus results in an increased tendency to form inclusions at a given growth rate. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy reveals the inclusions are metallic cadmium. For a reservoir temperature of 850°C inclusions were formed even at growth rates as low as 0.2 cm/hr.

Ampule rotation at constant velocity, ~17 rpm, is found to result in the formation of inclusions near the periphery and near the center of the crystal. This behavior may be attributed to the formation of boundary layers with diffusion dominated mass transport, and subsequent breakdown due to constitutional supercooling.

Thesis Supervisor: August F. Witt
Title: Professor of Materials Science
# Table of Contents

Acknowledgements ........................................ 13

Chapter 1 Introduction: Motivation ..................... 16
  1.1 Significance of CdTe .............................. 16
  1.2 Previously Identified Problems .................... 17
  1.3 Present Study ...................................... 17

Chapter 2 Background: Literature Survey ............... 21
  2.1 General Properties of CdTe ...................... 21
  2.2 Defects in CdTe .................................. 23
    2.2.1 Electrically active defects .................. 23
    2.2.2 Dislocation structure of CdTe ............... 25
    2.2.3 Polytypism and twinning ..................... 29
    2.2.4 Precipitates in CdTe ......................... 33
  2.3 Previously Employed Growth Methods and Results 35
    2.3.1 Melt growth techniques ....................... 36
    2.3.2 Solution growth techniques ................... 39
  2.4 Furnace Design and Modeling ...................... 41
  2.5 Summary ........................................ 45

Chapter 3 Approach and Structure ...................... 48

Chapter 4 Furnace Design ................................ 51
  4.1 Heat Transfer Control ............................ 53
    4.1.1 Furnace dimensions .......................... 54
4.1.2 Alignment and mechanical stability ........................................ 54
4.1.3 Design and construction of a high temperature isothermal zone .... 61
4.2 Vapor Pressure Control ......................................................... 73
  4.2.1 Mass transport considerations ..................................... 73
  4.2.2 Determination of the proper $P_c$ conditions ..................... 78
4.3 The Hardware ............................................................... 82
4.4 The Software ............................................................... 86
4.5 Results ............................................................................. 93
  4.5.1 Interface position ....................................................... 93
  4.5.2 Interface curvature ................................................... 97
  4.5.3 Sensitivity of interface position to fluctuations in reservoir zone
temperature ................................................................. 102

Chapter 5 Experimental Procedure ........................................ 105
5.1 Crystal Growth Methods .................................................. 105
  5.1.1 Material purification and charge preparation ....................... 105
  5.1.2 Ampule design and preparation ..................................... 107
  5.1.3 Seeding and necking .................................................. 110
  5.1.4 Vapor pressure control ............................................... 111
5.2 Materials Characterization Techniques ............................... 112
  5.2.1 Chemical etching ...................................................... 113
  5.2.2 Infrared microscopy .................................................. 118
  5.2.3 InfraRed spectroscopy .............................................. 119
  5.2.4 Electrical measurements .......................................... 120
  5.2.5 Electron microscopy ................................................ 121
  5.2.6 X-ray techniques .................................................... 125

Chapter 6 Results and Discussion ........................................ 127
6.1 Doping Effects ............................................................... 127
6.2 The Effect of Growth Velocity .......................................... 131
6.2.1 Results .................................. 131
6.2.2 Discussion .............................. 131
6.3 The Influence of Reservoir Zone
Temperature .................................. 135
6.3.1 Results ................................. 135
6.3.2 Discussion ............................... 137
6.4 The Effect of Ampule Rotation .... 143
6.4.1 Results ................................ 143
6.4.2 Discussion ............................... 144
6.5 The Influence of Seed Orientation .. 151
6.5.1 Results ................................ 151
6.5.2 Discussion ............................... 154
6.6 Effects of Ampule Coating .......... 160
6.7 The Effect of Changes in Thermal
Environment .................................. 160
6.7.1 Results ................................. 161
6.7.2 Discussion ............................... 163

Chapter 7 Analysis and Conclusions 167
7.1 A Discussion of Twinning in CdTe . 167
7.1.1 A theoretical basis for twinning in
ionic semiconductors ....................... 167
7.1.2 Twinning and its effect on electrical
properties ................................... 173
7.2 Origins of Polycrystallinity in CdTe . 179
7.3 The Nature of Precipitates in CdTe .. 180
7.4 Optimized Growth Conditions for CdTe . 183

Chapter 8 Summary and Suggestions for Future
Work ............................................ 187
8.1 Summary .................................. 187
8.2 Suggestions for Future work ....... 189

Appendix A Partial Vapor Pressure Calculations 192
Appendix B  Calculation of PID Constants  196

Appendix C  Derivation of the Feedforward Ramp Algorithm  199

Appendix D  Determination of Infinite Lengths  201

Appendix E  Selected Thermophysical Properties  203
   E.1 For CdTe . . . . . . . . . . . . . . . . . . . . . . . . 203

Appendix F  Determination of the Rotational Relation between Crystals  205

Appendix G  High Order Twinning  208

Appendix H  Measurement of Temperature Profiles  211

Appendix I  The Furnace Control Program  216
List of Figures

Figure 2.1: Phase diagram for CdTe .......................... 22
Figure 2.2: ZincBlende structure ............................... 27
Figure 2.3: Wurtzite structure ................................. 28
Figure 4.1: The 'Phoenix' furnace system ...................... 51
Figure 4.2: Schematic diagram of the 'Phoenix'
  furnace system interior ....................................... 58
Figure 4.3: Predicted temperature profile obtained
  with and without exostructure ............................... 59
Figure 4.4: Schematic X-section of modified furnace
  design ....................................................... 60
Figure 4.5: Finite element grid used for
  calculations ............................................... 66
Figure 4.6: Comparison of calculated and actual
  temperature profiles ....................................... 67
Figure 4.7: Heat input required to maintain an
  isothermal temperature profile in the central
  furnace cavity ............................................. 68
Figure 4.8: Comparison of the predicted profiles
  for two heater designs ................................... 69
Figure 4.9: Temperature profile obtained using a 2
  element heater ............................................. 70
Figure 4.10: Damping of interzone communication .............. 71
Figure 4.11: Sensitivity of the internal
  temperature profile on the reservoir zone
  temperature .................................................. 72
Figure 4.12: Comparison of predicted fluid flow in
  CdTe and Ge ................................................. 77
Figure 4.13: Vapor pressure data ................................ 81
Figure 4.14: Schematic overview of the 'Phoenix' furnace system ........................................ 85
Figure 4.15: Open loop system response for a step change in signal voltage to the power supply ... 89
Figure 4.16: Steady state temperature as a function of signal voltage .................................... 90
Figure 4.17: Typical furnace behavior ....................................................................................... 91
Figure 4.18: Typically observed set-point overshoot .................................................................. 92
Figure 4.19: Temperature profiles obtained using the evacuated bicylindrical thermal probe and a model charge ............................................................ 96
Figure 4.20: Initial meltback interface shape ............................................................................. 99
Figure 4.21: IR macroscopy of Ag doped CdTe experiencing an increase in growth rate from 0.2 cm/hr to 2.0 cm/hr ......................................................................................... 100
Figure 4.22: FTIR analysis of Ag doped CdTe which has experienced a growth rate change from 0.2 cm/hr to 2.0 cm/hr ......................................................................................... 101
Figure 5.1: Ampule Design for VPC CdTe Growth ................................................................. 108
Figure 5.2: Ampule Attachment Mechanism ........................................................................... 109
Figure 5.3: Stria tions in LEC CdMnTe revealed by etching ....................................................... 114
Figure 5.4: Decorated dislocations terminating at etch pits ..................................................... 115
Figure 5.5: Montage of dislocation networks revealed by etching ............................................ 116
Figure 5.6: Montage of networks revealed by X-ray topography ............................................ 117
Figure 5.7: TEM specimens produced using different methods. A: Chemical Polish B, C: Ion Milling ................................................................. 124
Figure 6.1: Infrared spectra obtained on Ag doped CdTe ......................................................... 129
Figure 6.2: IR microscopy of Ag doped CdTe ................................................................. 130
Figure 6.3: The effect of changes in growth rate on microstructure A = 0.2 cm/hr: B = 0.6 cm/hr: C = 1.2 cm/hr: D = 1.2 cm/hr ............... 133
Figure 6.4: Initiation of polycrystalline growth due to a lowering rate changed from 0.2 cm/hr to 2.0 cm/hr ............... 134
Figure 6.5: The effect of variations of reservoir zone set point ............... 139
Figure 6.6: Scanning transmission electron microscopy data of a Te precipitate ............... 140
Figure 6.7: Electrical properties as a function of reservoir zone temperature ............... 141
Figure 6.8: Near and mid IR absorption coefficients ............... 142
Figure 6.9: Fluid flow analysis with and without rotation ............... 146
Figure 6.10: Correlation of external pits with reservoir temperature change ............... 147
Figure 6.11: IR microscopy of the periphery and center of a boule grown with rotation ............... 148
Figure 6.12: A: CdTe crystal growth with rotation and Cd added to reservoir B: Expanded view of last to the freeze portion ............... 149
Figure 6.13: Metallic inclusions ............... 150
Figure 6.14: The effectiveness of a reduced diameter channel for grain selection ............... 156
Figure 6.15: Grain selection resulting from the use of a graphite aperture ............... 157
Figure 6.16: [110] Seeded growth of CdTe ............... 158
Figure 6.17: [111] Seeded growth ............... 159
Figure 6.18: Crystal grown with interface near cooler ............... 165
Figure 7.1: Insitu phase transformation under electron beam irradiation ............... 172
Figure 7.2: A: IR micrograph of CdTe showing the alignment of dislocations to twin boundaries.
   B: Coincidence of etch pits of the opposite sense on a twin boundary. 178
Figure 7.3: Precipitates decorating dislocations in CdTe, using different sample tilts. 182
Figure B.1: Block diagram of furnace system and control 198
Figure G.1: Schematic representation of a second order twin 210
Figure H.1: Evacuated bicylindrical thermal probe 213
Figure H.2: Model charge used for temperature profiling 214
Figure H.3: Temperature profiles measured using different furnace ambients 215
List of Tables

Table 1: Thermocouple positions referenced to the top of the ampule support shaft in its upper position ........................................... 64
Table 2: Materials constants and furnace characteristics used for numerical modeling of fluid flow .................................................. 75
Table 3: Comparison of calculated and experimentally determined interface position ................................................................. 94
Table 4: Predicted interface relocation due to a ± 0.8°C Hot Zone Fluctuation ................................................................. 102
Table 5: Pauling electronegativities for the IIB and VIB elements .......................................................................................... 170
Table 6: Structures of II-VI compounds .................................................. 170
Table 7: Calculated Vapor Pressures for Cd and Te as a Function of Composition ......................................................... 195
Acknowledgements

I would like to express my sincere appreciation to Professor August F. Witt for his insistence on excellence, support, and encouragement through the years.

My deepest thanks go to Professor Shahryar Motakef for his patient tutelage in the field of heat transfer analysis. There is no doubt that this thesis has been vastly improved as a consequence of his contributions.

I am very grateful to Professor John B. VanderSande, who first stimulated my interest in materials science, for his support and guidance.

The contributions of Dr. Piotr Becla to my understanding of the art of crystal growth of II-VI semiconductors are deeply appreciated. Many thanks to Professor Kui-Hong Yao for his assistance in FTIR analysis.

I would like to thank Professor Bob Ogilvie for his advice in the application of X-ray techniques. Discussions with Professor Robert Balluffi and Dr. Thomas Bamford concerning the determination of the relative orientation between grain boundaries were greatly appreciated. My thanks go to Dr. Zia Vafa for his expert advice and discussion concerning furnace control. The contribution of seeds from Dr. Don Hobgood of Westinghouse and Dr. Luigi Columbo of Texas Instruments was most appreciated. Many thanks to Patrick Griffin for conducting the numerical fluid flow analysis.

I would also like to express special thanks to the members of the electronic materials group for their help during the course of this work. To Dr. Michael Wargo for many helpful discussions, to Dr. David Mattheisen for
conducting interface demarcation studies in the 'Phoenix', to soon-to-be Dr. Douglas Carlson for developing IR imaging techniques and illuminating important political issues, to John DiFranchesco and Joe DiMaria for their technical support. Thanks goes to Gloria Landahl for keeping things running smoothly for all of us, all these years. She has consistently been a source of good cheer and encouragement.

To my friends at MIT: you have made life here immeasurably more enjoyable. Best wishes to all of you, or perhaps more importantly, Godspeed.

To my parents Spiros and Evelyn go my deepest love, respect and gratitude. Your love and support have been a constant source of inspiration and strength to me.

To my beautiful wife Karen and wonderful daughter Julia I dedicate this document and myself. You are the most precious gifts that life has to offer. Thinking of you makes me realize how truly fortunate I am.
Chapter 1

Introduction: Motivation
1.1 Significance of CdTe

CdTe is an important II-VI compound semiconductor. It is the only II-VI semiconductor that can be produced n-type, p-type, or with high resistivity. Demonstrated applications for this material include⁴,⁵,⁶:

- Solar cells
- Room temperature x-ray detectors
- γ-ray detectors
- Electro-optic modulators
- Nonlinear optical devices
- Optical elements for infrared applications

Presently CdTe is widely used as a substrate⁷ for epitaxial growth of HgCdTe, the primary IR detector material for the 8-12 micron region. It is well known that the quality of epitaxial layers is ultimately dependent on the quality of the substrate. The epitaxial layers can be degraded by diffusion of impurities, or the propagation of dislocations, grain boundaries or twins, from the substrate. Problems associated with these defects are manifested in the form of low device yield, or poor device performance. The poor quality of bulk CdTe has prompted attempts at epitaxial growth on other substrates⁸,⁹ with more mature technologies, such as GaAs and InP, with only limited success. Another promising application for CdTe is for the generation of tunable coherent radiation in the infrared, a portion of the spectrum for which few sources exist. By adjusting the spacing of lamellar twins, it has been shown⁸,⁹ that enhanced
second harmonic generation occurs in CdTe. Understanding and ultimately controlling defect formation is therefore critical if further development of this technology is to occur.

1.2 Previously Identified Problems

CdTe single crystals have been prepared using melt growth, solution growth, and vapor growth techniques. Both bulk growth and epitaxial growth of CdTe have been attempted. Analysis of the crystals produced has identified twins, grain boundaries, precipitates, inclusions, dislocations, and point defects as the prevalent defects. The cause of these defects is not well understood. However it is suspected that they are a result of either one or a number of the following.

- Lack of control over the stoichiometry during high temperature processing.\textsuperscript{10,11,12,13}

- Lack of control over the heat and mass transfer during crystal growth.\textsuperscript{14}

- Kinetic effects related to crystallographic anisotropy.\textsuperscript{15}

- Impurities either in the starting material or introduced during subsequent processing.\textsuperscript{16,17,18}

- Thermal or mechanical stresses present during crystal growth processing.\textsuperscript{19}

1.3 Present Study

A limitation of previous studies pertaining to the bulk growth of CdTe results from an inability to control enough variables in the growth process. Results of Wang et.
al.\textsuperscript{20} indicate that the growth rate for a conventional Bridgman furnace is always transient and never equal to the lowering rate. Furthermore it was found that the furnace behavior was critically dependent on the location of the control thermocouples. These results help explain the difficulties associated with comparing results obtained from different furnaces. In the present study a vertical Bridgman/Stockbarger furnace system was designed providing well defined boundary conditions based in part on the work of C. Wang\textsuperscript{21}. In addition the design incorporates a third actively controlled, heatpipe based, zone to control the composition of the liquid. The furnace is of modular design, accommodating major changes in furnace characteristics, which allows a wide range of furnace parameters to be examined. The design allows reproducible seeding to a well known crystallographic orientation. These technological advances allow the simultaneous control of the heat transfer, the orientation, and the composition. Furthermore, the well defined boundary conditions allow numerical and analytical modeling of the system.

Characterization of the impurity content of the material was obtained using spectrographic analysis, Hall effect measurements, resistivity v.s. temperature measurements, and optical absorption measurements. Recent theoretical analyses by Motakef\textsuperscript{22,23} have indicated that stress in vertical Bridgman is predominantly due wetting of the ampule and subsequent differential expansion. In the present study wetting was modified by careful cleaning procedures and by pyrolytic graphitization of the ampules. IR microscopy was used to evaluate the macroscopic distribution of precipitates and inclusions. STEM analysis was used to identify the elemental composition of the precipitates, while EDX analysis identified the inclusions formed. Characterization of the crystalline perfection was
accomplished using a grain boundary and twin revealing etch. The relative orientations between grains were determined using Laue back reflection.

In summary, the thrust of this study was to provide a systematic analysis of the effects of the various adjustable parameters of crystal growth on the defect structure of CdTe. The results were obtained in a manner which could accommodate comparison with results from other furnace designs with well defined boundary conditions. The ultimate goal of this work was to provide a set of relationships which could be used to optimize growth conditions for a desired set of materials properties.
Chapter 2

Background: Literature Survey
2.1 General Properties of CdTe

Cadmium Telluride is a compound semiconductor which crystallizes in the zincblende ( sphalerite) crystal structure. The structure belongs to the space group F\bar{4}3m (T\bar{4}g), and can be considered as two interpenetrating FCC lattices which have a relative displacement of a/4[111], where a is the unit cell edge length. Cadmium atoms occupy the lattice sites on one of the FCC sublattices while Tellurium atoms occupy the sites on the other sublattice. The lattice parameter, a, is a function of the composition of the solid. It has been reported as 6.482 Å for crystals grown from stoichiometric melts. Lattice constants of 6.480 Å have been measured for crystals grown from Cd rich solution and 6.4888 Å for Te rich solution growth\textsuperscript{24}. Unlike in the case of the diamond cubic structure, the zincblende structure does not have a center of inversion symmetry along the [111]. This lack of inversion symmetry leads to piezoelectric, piezobirefringent, and electrooptotic effects. The Cd–Te bond length has been measured at 2.80 Å, while the Cd–Cd distance is 4.58 Å\textsuperscript{25}.

The density of solid CdTe has been reported\textsuperscript{26} as 5.86 gm/cc at 300 K. It has a congruent melting point\textsuperscript{27} of 1092°C, corresponding to a Te composition of 50.089%. The liquidus phase diagram has been compiled, based on the work of deNobel, Lorenz, Kulwicki, Steininger, and Brebrick, by Strauss\textsuperscript{28}. Zanio\textsuperscript{1} has constructed the solidus existence region based on the work of deNobel and Smith. The temperature v.s. composition phase diagrams are presented in Figure 2.1. Select thermophysical properties for CdTe will be presented in appendix E.
Figure 2.1: Phase diagram for CdTe
2.2 Defects in CdTe

The following section contains a summary of the defects which have been reported for CdTe. The review is included to provide insight as to the sources attributed to generation of these defects. Furthermore, it will serve to point out that defect identification in CdTe is still an area of considerable controversy in need of more extensive research.

2.2.1 Electrically active defects

DeNobel\textsuperscript{19} was the first to propose a defect model for CdTe. The model is based primarily on room temperature Hall effect and conductivity measurements, obtained from samples which had been annealed under controlled cadmium partial pressure, i.e. $P_{\text{Cd}}$. A correlation between the conductivity type and the partial vapor pressure of Cd during annealing was observed. DeNobel concludes that the electrical properties of CdTe are dominated by native defects, which he identifies as Cd\textsubscript{i} and V\textsubscript{Cd}.

An implicit assumption in deNobel's work was the requirement that the high temperature defect structure be 'frozen in' at room temperature. The validity of this assumption was questioned when the room temperature conductivity was found to change with time\textsuperscript{29}. High temperature measurements\textsuperscript{18,10,11,12} showed a conductivity independent of $P_{\text{Cd}}$ for specimens at low $P_{\text{Cd}}$, while those at high $P_{\text{Cd}}$ were dependent on $(P_{\text{Cd}})^{1/3}$. Clearly the singly ionized native defects proposed by deNobel could not explain this behavior, furthermore the room temperature defect
structure is evidently quite different from the high
temperature structure.

Smith\textsuperscript{a} concludes that doubly ionized native donors
dominate the conduction at high $P_{c4}$. The conclusion is based
on high temperature Hall effect and conductivity
measurements. In these measurements he found $n \propto (P_{c4})^{1/3}$
and the carrier concentration increased with temperature.
For low $P_{c4}$ the carrier concentration was independent of $P_{c4}$,
and only slowly varying functions of temperature. At low
temperatures the conduction was p-type, however heating the
samples to between 350 and 700\textdegree{}C resulted in type conversion.
These results suggest that the low temperature behavior is
dominated by acceptor impurities. The type inversion can be
understood by recognizing that the intrinsic carrier
concentration increases with temperature and the mobility of
electrons is greater than that of holes.

Chern et. al\textsuperscript{10} proposed a model of the defect
structure which attempts to reconcile the electrical
properties at both room and high temperature. Considering a
plausible energy level diagram, they concluded that trapping
alone could not account for the discrepancy between the room
and high temperature electrical behavior. Precipitation of
native donors however was invoked to reconcile the observed
differences.

An alternative to the native defect domination of the
electrical properties has been proposed by Pautrat et. al\textsuperscript{17}.
The model postulates that the electrical properties of II-VI
compounds are dominated by impurities. These impurities are
thought to segregate to Te rich precipitates, the last to
freeze liquid. Annealing causes dissolution of the
precipitates due to the enhanced solubility of Te at high T,
and to the indiffusion of $V_{\text{Te}}$. The impurity is then released
into the matrix, and rapidly diffuses throughout.
Another proposal suggests that the change in stability of certain sites occupied by amphoteric impurities determines the electrical properties.\textsuperscript{30} For example Si, which is a common impurity in CdTe, is a donor on Cd sites and an acceptor on Te sites. The ratio of Si on Cd sites to Si on Te sites is expected to be a function of the ratio of the concentrations of vacancies on these sites, and as such a function of $P_C$. Unfortunately, little is known about the behavior of Si in CdTe.

Point defects are not the only defects which have been linked to electrical activity. Hirth and Ehrenreich have postulated the electrical activity of dislocations in II-VI compounds.\textsuperscript{31} Using similar reasoning one would also predict the electrical activity of grain boundaries. The photoplastic effect observed in CdTe provides experimental support for these contentions. Furthermore, the presence of dislocations and grain boundaries provide heterogeneous nucleation sites for precipitation, and paths for enhanced diffusion of electrically active impurities.

\subsection*{2.2.2 Dislocation structure of CdTe}

The primary slip system is the \{111\} <110>, with a perfect dislocation Burgers vector of $a/2\langle110\rangle$. There are two different types of glide dislocations the so called glide set and shuffle set. The differences between them can be best understood by recalling that the stacking sequence along [111] in the zincblende structure can be represented by $\ldots aBbCcAaBbCcA \ldots$, see figure 2.2. The glide set represents dislocation which terminates on broken aB type bonds. The shuffle set represents a dislocation which terminates on broken bB type bonds\textsuperscript{32}. The results of Hall and VanderSande\textsuperscript{33} indicate that only the glide set exist in CdTe. They also have determined the equilibrium stacking fault
energy for CdTe to be 10.1 ± 1.4 erg/cm², by measuring partial dislocation separations. At elevated temperatures (500°C) evidence for extensive thermally activated recovery was observed. Specimens deformed to high strain levels at 500°C showed extensive formation of subgrain boundaries of varying degrees of misorientation. The samples showed little work hardening at this temperature²⁴.

The source of dislocation formation in CdTe has been identified as stress introduced either due to differential contraction upon cool down, or due to nonlinearity in the thermal field²³. In Bridgman however, ampule wetting and differential contraction is thought to dominate. In cases where the growth is far removed from stoichiometric conditions, dislocation formation may also be due to coalescence of point defects³⁴.

Chern and Kroger¹⁰ have determined the self diffusion behavior of various point defects in CdTe, utilizing tracer diffusion studies. They find that:

\[ D^* = D_0 \cdot P^a \cdot \exp(-H/kT) \text{ cm}^2/\text{sec} \]

where:

\( D_0, a, \) and \( H^* \) are functions of the defect type, and stoichiometry.
Figure 2.2: ZincBlende structure

Stacking of (111) Planes in ZincBlende

$\text{a} = 6.482 \text{ Å}$
Figure 2.3: Wurtzite structure

c = 7.47 Å

a = 4.57 Å

- 28 -
2.2.3 Polytypism and twinning

The observation of polytypes in II-VI compound semiconductors is well documented\textsuperscript{3,4}. In particular, both a zincblende (figure 2.2) and wurtzite (figure 2.3) phase (space group $P\overline{6}_3mc C\overline{4}v$) exist at room temperature in ZnS. The differences between zincblende and wurtzite are analogous to the differences between FCC and HCP (i.e. in zincblende the stacking sequence along a $<111>$ is ...aAbBcCaAbBcC... while in wurtzite it is ...aAbBAbB... along the $<0001>$). ZnS is also known to exist in forms that are faulted, i.e. intermediate between the cubic and hexagonal forms. In cases where the faults form a periodic array, stacking sequences which reflect this periodicity can be defined, these are called polytypes. At least 7 different polytypes have been identified for ZnS. In CdTe, polytypes have not been observed for standard conditions, however they have been reported for thin films\textsuperscript{37,38}. The most prevalent polytype in these thin films is wurtzite.

Twining is frequently observed in CdTe crystal growth\textsuperscript{19,27,39,15}. Twinning in the zincblende structure is commonly described as a 180° rotation about a $<111>$ or a ± 60° rotation about the same axis. However, 24 different axis-angle pairs can be used to describe the crystallographic operation in cubic systems\textsuperscript{40}. These correspond to 4 physically distinct twins, with their composition planes perpendicular to $<111>$. In the sphalerite crystal structure however, some of the 24 twinning descriptions yield a paratwin configuration\textsuperscript{41}. The paratwin is equivalent to a mirror plane and results in bonds between like atoms. Due to the unfavorable energetics involved it is unlikely that the paratwin configuration exists in nature. Indeed, it has never been observed experimentally. Therefore, the term twin...
is usually taken to mean the rotational orthotwin configuration.

The work of Vere et. al.\textsuperscript{42} which included high temperature deformation experiments to 1000°C, concludes that twin formation in CdTe is not due to mechanical stress. This conclusion was supported by the lack of twin propagation into the seeds of LEC crystals with high twin densities. Other high temperature deformation studies also failed to report any nucleation of twins or propagation of twins\textsuperscript{34}. Twinning is therefore generally believed to be of the growth twinning variety. A discussion of the mechanisms involved in deformation related twinning will therefore be neglected. For a discussion of the differences between growth and deformation twinning as well as a variety of other twinning forms, the reader is directed to the review paper by Cahn\textsuperscript{43}.

The causes of growth twinning which have been suggested to date include:

1. Melt-Solid interface orientation

2. Melt-Solid interface morphology: Heat transfer

3. Growth rate: Kinetic undercooling

4. Crystallographic structure effects: Polarity effects

5. Stoichiometric effects and impurities

An early theoretical model of the twinning process by Billing\textsuperscript{44} concluded the probability of twinning increased with the degree of alignment of the resulting \{111\} planes with the growth axis. The author uses the above rational to predict that \{100\} type seed would most likely lead to twinning. Bolling et. al.\textsuperscript{45} correlate increased twin density, in Germanium, with supercooling, either absolute or constitutional. They observed the most favored growth axis
was of the family \((h,h,-1,1)^n\), which are perpendicular to the (111) family of planes. For material which was doped with Ga the tendency to twin increased, due to the constitutional supercooling. The system was less prone to twinning for a large thermal gradient/growth rate ratio, more planar interface. The thermal field in front of the growth interface was found to experience absolute supercooling for large growth rates, and increased twinning was observed under these circumstances.

In his thesis, Szilagyi\(^5\), discusses two twinning mechanisms, thermally determined or constrained twinning, and growth accident or random twinning. Constrained twinning, would occur if it resulted in exposure of a surface with a larger number of dangling bonds. Surfaces with large numbers of dangling bonds were thought to decrease the kinetic undercooling associated with propagation of new layers. Growth accident twinning, was described in terms of the formation of 'twin nuclei', i.e. clusters in the melt, and their attachment to the growth interface. This phenomenon is more likely to occur in systems with highly associated melts, those retaining a large fraction of covalent bonding. Szilagyi calculates the minimum stable cluster size based on a residual dangling bond density criterion. The model assumes that a cluster is not stable unless the residual dangling bond density per atom is less than 2. The smallest cluster for which this occurs is equivalent to a twinned configuration for the zincblende structure.

Of critical import in the constrained twinning model is the method used to calculate the density of dangling bonds as a function of orientation. In particular the assumptions on which it is based are as follows.

- All bonds are \(sp^3\) hybridized
- No surface relaxation or reconstruction is considered
- No polarity effects are considered
- All orientations can be constructed using a linear combination of \{111\} and \{100\} type steps
- The \{100\} contribute 2 dangling bonds/atom, while the \{111\} contribute 1 dangling bond/atom

Using a formulation based on these assumptions Szilagyi was able to generate a plot of constant density contours, which he used to predict growth directions which were stable against twinning. His theory suggests that growth with an interface which does not deviate by more than 24.1° from a \{100\} would be stable against confined twinning. The potential for accidental twinning due to cluster attachment, however, is not affected by orientation.

Mackenzie and Nicholas\(^7\) determine the density of broken bonds in the diamond cubic structure. Their assumptions are different than those of Szilagyi, which affects their dangling bond densities. These authors assume a planar cleavage surface in contrast to the \{111\}, \{100\} steps in the previous model. They also assume that there are three broken bonds/atom associated with the \{111\}. Despite the apparent differences in the model, these authors also suggest that the density of dangling bonds for the low index directions is highest in the \{100\} directions. Therefore, based on these results one would also expect that \{100\} growth would be most favorable to twin free growth, if kinetic undercooling minimization is the driving force for twinning.
2.2.4 Precipitates in CdTe

Many workers\textsuperscript{18,10,48,49} have invoked the formation of precipitates to explain the electrical behavior of CdTe. Other experiments have also suggested precipitates were being formed in CdTe.\textsuperscript{30,31} Predictions based on the retrograde solidus of the phase diagram also anticipate the formation of precipitates. However, little has been done to identify these defects either chemically or structurally. The following section is a summary of the pertinent studies which examine precipitates in CdTe.

Shin et. al.\textsuperscript{32} observed a large number of inclusions, which were between 3 and 15 µm, in diameter using optical microscopy. Spatially resolved Auger measurements on these inclusions indicate that they are predominantly composed of Te. X-ray diffraction revealed extra peaks which were assigned to a high pressure Te phase. Several peaks which were observed could not be assigned, their source remaining unknown. Raman spectroscopy yielded results similar to those obtained for Te single crystals, however there were peak shifts observed. The shifts in the Raman spectrum were attributed to the fact that the Te inclusions existed in the high pressure structure, not the standard structure. Annealing in Cd rich atmospheres at temperatures between 600-800°C yielded a reduction in the density of smaller inclusions, however the larger inclusions remained unaffected.

Magee et. al.\textsuperscript{33} examined Cl and In doped samples which were oriented (111) with TEM. Specimens were annealed in a Cd rich atmosphere at temperatures between 100 - 900 °C for periods of 1 - 48 hours. The anneal was conducted in a single zone furnace, which did not allow for the precise control of $P_{\text{Cd}}$. The presence of diffuse Te rings in the
diffraction pattern are noted, however no other precipitate spots are reported. Determination of precipitates other than Te was accomplished by measuring Moire fringe spacings. Te, In$_2$Te$_3$, and CdCl$_2$ precipitates are reported. The Te precipitate size was found to be ~60Å in diameter, annealing to $\geq 500^\circ$C eliminated all evidence of Te precipitates. In several samples stacking faults are reported. They were found to increase in both size and density with short term annealing. In regions of stacking fault growth, dislocation loops of 1000 - 1500 Å diameter are reported and determined to be due to vacancies.

Selim et. al.* have observed precipitate formation in nominally undoped and In doped CdTe which has been annealed in atmospheres of various $P_{\text{Cd}}$. For nominally undoped material, which was found to contain $5 \times 10^{16}$ cm$^{-3}$ of Cl, precipitate formation was observed for crystals quenched after annealing at 900°C with $P_{\text{Cd}} = 2$ atm. Analysis of the precipitates was not possible since no perturbation of diffraction pattern was observed. For crystals cooled after anneals at 700°C with $P_{\text{Cd}} = 2 \times 10^{-2}$ atm dislocation loops were observed and identified as prismatic interstitial loops with Burgers vector of the type $a/2[110]$. The authors believe this suggests Cd$_4$ precipitation. For In doped material the quenching sequence as well as the annealing temperature was found to affect precipitate density. Samples annealed at 700°C with $P_{\text{Cd}} = 5 \times 10^{-2}$ atm did not form precipitates. For samples annealed to 800°C, which experienced similar conditions, precipitates were observed when the ampules were quenched such that the reservoir was cooled last. However, if the Cd reservoir was quenched before the crystal no precipitates were observed. Since the carrier concentration of these samples dropped below the In concentration, the authors suggest the precipitates are a CdIn alloy. Annealing this material to 700°C with
$P_{c_4} = 5 \times 10^{-3}$ atm resulted in the formation of vacancy type dislocation loops. These were suspected of being formed due to coalescence of $V_{c_4}$ based on theoretical considerations.

Narayanan and Rustomji have attempted to verify a model proposed by Selim and Kroger for the defect structure of P doped CdTe. Utilizing TEM they analyzed both as grown and annealed CdTe of varying P content. A dispersion of fine precipitates 100 – 300 A whose volume fraction decreased with decreasing [P] was observed in material grown horizontal Bridgman. For annealed material microstructural changes were observed both as a function of [P] and $P_{c_4}$. At low $P_{c_4}$ microvoids were observed, the size and density increased with increasing [P]. Careful examination of the voids revealed them to be partially filled with a precipitate phase. Analysis of the void-precipitate complexes was not possible since there was no evidence of their existence in the diffraction patterns obtained. They were identified however, on the basis of the proposed defect model, as Te precipitates. Increasing the $P_{c_4}$ was found to decrease the size and density of the void-precipitate complexes. The material containing the greatest concentration of P was found to form extremely fine precipitates after anneals at high $P_{c_4}$. These could not be identified either, but on the basis of the defect model were thought to be clusters of Cd$_4$.

2.3 Previously Employed Growth Methods and Results

The following section contains a summary of select bulk growth techniques. Neglecting discussion of epitaxial techniques can be justified, since they require substrates which are almost invariably produced by bulk growth techniques. The bulk techniques can be classified into two major groups, those from near congruent melts and solution
growth. In the interest of brevity, this discussion will be limited to novel techniques, i.e. those providing an improvement over standard techniques.

2.3.1 Melt growth techniques

The melt growth methods include, vertical and horizontal Bridgman and Stockbarger, zone refining, and liquid encapsulated Czochralski (LEC) techniques. In general, melt growth techniques offer the advantage of high speed growth since mass transport is not a severe limitation. Czochralski techniques have the additional advantage of having a free surface which eliminates problems associated with a containment. The usually larger axial thermal gradients present in LEC growth permit the use of higher growth rates. Bridgman/Stockbarger has the advantage of better defined thermal boundary conditions with greater opportunity for their control. While zone refining can be used to purify the material in situ.

LEC crystals have been produced by a number of groups\textsuperscript{4,5,5a}, however the quality has not been as good as that attainable using other techniques. In all cases, the growth of ingots of diameter greater than about 1 cm was problematic. All boules were polycrystalline, and difficulty with diameter control was noted. The most successful application of LEC to date was conducted by Hobgood et al.\textsuperscript{5a}, who were able to grow 50 mm diameter CdTe boules by increasing the axial gradient to \( \sim 400^\circ\text{C/cm} \) in the vicinity of the interface. In parallel they included a water cooled cold finger at the base of the crucible in order to influence the radial heat transfer. Regardless, they were unable to produce single crystals of CdTe, and experienced very heavy twinning. The maximum grain size was on the order of 1 cm in linear dimension. By addition of MnTe up to 0.20 mole
fraction, Hobgood was able to grow single crystalline material. The crystal had twin lamellae perpendicular to the \langle111\rangle growth axis. The lamellar region did not extend to the edge of the boule which was polycrystalline. The incorporation of boron inclusions was also reported, as are etch pit densities of approximately $10^6$/cm$^2$.

Favorable results have been obtained using other techniques. Much of the early work utilized a horizontal Bridgman configuration\textsuperscript{37,38} to control the vapor pressure over the melt. Kroger and deNobel report the production of single crystals with twins using a seeded arrangement. Occasionally crystals without twins were produced. Unfortunately, no correlation between growth conditions, i.e. reservoir temperature, and electrical properties is presented. Lorenz demonstrates the effectiveness of vapor pressure control in the horizontal Bridgman configuration. He was able to produce single crystals which were up to 5 cm in length. Twinning was reported, however no electrical data on as grown material is presented. Lorenz was also able to produce crystals by heating the liquid, when the $P_c$ was high enough. More recently\textsuperscript{39}, horizontal Bridgman, without vapor pressure control, has been used to produce crystals 5 cm diameter and up to 80% single crystalline. Low dislocation densities $5 \times 10^4$/cm$^2$ using the Nakagawa etch were reported.

Zone refining has been applied to the CdTe system in both horizontal\textsuperscript{40} and vertical\textsuperscript{41,42} configurations. Woodbury and Lewandowski\textsuperscript{43} grew crystals up to 10 cm$^3$ using vertical zone refining by superimposing oscillations on the ingot during the last zone pass. They also observed a correlation between the susceptor temperature and the conductivity type, with $p$-type conduction for higher, $\geq 1200^\circ$C, susceptor temperatures. Triboulet and Marfaing\textsuperscript{44} however failed to observe any correlation with susceptor temperature finding instead that the conductivity was
dominated by the starting material. Impurities observed by ionic probe included Al, Na, Cl, F, K, Co, Fe, and Si. Mass spectrometry indicated rather large concentrations of C, while emission spectroscopy revealed Si, Ca, Mg, Cu, Fe, and Ag. Single crystals of between 2-3 cm³ are reported, as are high mobilities of ~10⁵ 35K.

Prokof'ev and Rud⁶⁰ report the growth of 15 cm long single crystals, i.e. 75% of the boule length, using the horizontal zone refining method. A dependence of crystal quality on vapor pressure and growth rate was observed. For high Cd partial pressure, porous material was produced. Intermediate values of P₀ yielded solid bars with a preponderance of twins, increasing growth rate from 0.5 to 1.5 cm/hr was found to decrease twinning. Partial vapor pressures of Cd between 0.8 - 1.2 Atm produced material which was generally free of twins. Decreasing the gradient from 20°C/cm to 12°C was found to decrease the yield of single crystals and increase the tendency to twin.

The most extensively used methods for the production of CdTe crystals to date have been the vertical Bridgman⁷⁵ and Stockbarger⁶⁶ techniques, a review of the early work is in Zanio¹. Yamada⁶⁷ utilized capillary tubes to enhance the likelihood of single crystal formation. Ampules with a conical shape have also been employed to facilitate nucleation of a favorable orientation⁶⁸. Seeded growth in the vertical Bridgman method has not as yet been reported. Soft-mold growth⁷⁹ using a B₂O₃ encapsulated ampule has been attempted with an apparent decrease in dislocation density, approximately 10⁴/cm². Dislocation densities as low as 10²/cm² have, however, been reported by Kyle⁸⁰ without the use of soft-mold techniques.

Attempts at controlling the stoichiometry have ranged from adjusting the starting composition of the
charge\textsuperscript{70,71,72,73} to controlling the temperature of a portion of the ampule\textsuperscript{64}. Kyle\textsuperscript{39} has employed a reservoir zone to maintain a constant $P_{c4}$ over the melt in the Bridgman configuration. His findings suggest that the liquid above the melt does not impede communication of the melt-solid interface with the reservoir zone. The production of n-type CdTe was reported for high, i.e. 2.6 atm, Cd partial pressures. Production of n-type material was not possible using standard quartz tubing however it was observed using synthetic tubes. The n-type material was not stable and type conversion was observed with time\textsuperscript{74}. Kyle also found the crystallinity degrades when $P_{c4}$ was much different than 1 atm, or the temperature gradient at the interface was below 20°C/cm. Large single crystals are reported however whole boule single crystals are not.

2.3.2 Solution growth techniques

The lower operating temperatures associated with solution growth eliminate some of the problems inherent with melt growth techniques including:

- Reduction of impurity incorporation from ampule dissolution

- Reduction in the concentration of native defects

- Ability to use alternative containment materials

- Potential growth below the retrograde portion of the solidus eliminating this source of precipitate formation

- Reduced solubility of impurities
Although in theory both Cd and Te rich solutions could be used, only Te rich solutions are in practice due to the limited solubility of CdTe in Cd, figure 2.1. Application of solution growth to the production of CdTe single crystals has been investigated by a number of groups. Isothermal solution growth\textsuperscript{79,84} has produced crystals which are quite small with facets forming on the (100) and (111) planes. Problems associated with constitutional supercooling, resulting in inclusion formation and ultimately interface breakdown, have precluded serious application of the technique to crystal growth. Improved crystal quality has been attained by using solution growth techniques which incorporate a temperature gradient. Zanio\textsuperscript{79} has produced boules of 80% single crystal as large as 25 cm\textsuperscript{3} using a cold finger technique. Infrared imaging of this material revealed the matrix to be inclusion free, however grain boundaries and twins were decorated with inclusions or precipitates. The traveling heater method (THM) has also been utilized to produce CdTe, resulting in crystals of several cubic centimeters\textsuperscript{76,77}. Although polycrystalline ingots were obtained at growth velocities of as high as 2 cm/day, however to obtain single crystals rates of less than 0.75 cm/day were required. The material quality, as measured by resistivity, was found to improve with decreased growth rate, as low as 0.3 cm/day. Wald and Bell\textsuperscript{78} have utilized forced convection by accelerated crucible rotation to impose reproducible convection in their system. They find that increased convection leads to a doubling of the critical growth rate, i.e. before the onset of inclusion formation. Tranchart and Bach\textsuperscript{79} utilize a gas bearing system to eliminate vibrations which can be introduced by motors. Using their system the authors note a larger fraction of the boules produced are single crystalline. Furthermore, Te inclusions are not observed except near the periphery of the boule.
2.4 Furnace Design and Modeling

A limitation of many classical experiments is a consequence of the use of furnaces with ill-defined thermal boundary conditions; resulting in an inability to adequately control the heat transfer of the system. More recently, a considerable amount of both theoretical and experimental work has been conducted to determine how to improve the controllability of heat transfer in the vertical Bridgman/Stockbarger furnace configuration. The results of these studies has had a profound influence on the design of the furnace used in the present study and will therefore be discussed albeit briefly.

Issues which are critical to the design of crystal growth systems relate to the sensitivity of the melt solid interface position and the interface shape on the temperatures of the adjacent zones. Concave interface curvatures have been associated\textsuperscript{80} with nucleation of grains at the ampule wall and subsequent polycrystalline breakdown for the crystal. Convex interface shapes are thought to enhance grain selection. However, large interface curvature has been associated with the formation of twins\textsuperscript{44,45,15}. This suggests planar or perhaps slightly convex interfaces would optimize single crystalline growth. Instability of the interface position with fluctuations in thermal environment correlates to an instability in microscopic growth rate. Well controlled growth rate is critical in producing single crystals of high quality. Excessive growth rates\textsuperscript{81} have long been known to cause interface breakdown. Understanding the relationship between furnace boundary conditions and the critical interfacial region is therefore extremely important.

Early theoretical work by Chang and Wilcox\textsuperscript{82} suggests that the incorporation of an insulating zone between
the heater and cooler increases the ratio of axial/radial heat transfer, thereby decreasing the sensitivity of interface shape on the thermal conditions. Their experimental results\textsuperscript{3} on Naphthalene indicate that the interface shape is not constant during the run but a function of the position in the boule. This illustrates the influence of end effects, typical of classical designs, in this system.

Ampule materials were examined numerically by Sen and Wilcox\textsuperscript{44}. Their findings suggest that the sensitivity of the interface location to fluctuations in thermal environment increases as the coupling between the furnace and ampule decreases. For high thermal conductivity material the sensitivity was minimized by using an ampule with high conductivity, while for materials of low conductivity an ampule of low conductivity gave the best results.

The effects of insertion of an insulating gradient zone on the furnace characteristics were modeled by Fu and Wilcox\textsuperscript{5} using finite difference techniques. Their findings suggest that the sensitivity of the interface shape on thermal environment decreases with increasing insulation thickness. All isotherms moved toward the cooler for the case of a moving ampule. The sensitivity of the interface shape and position to temperature fluctuations is calculated to be greater for the cooler than for the heater.

Wang, Witt, and Carruthers\textsuperscript{20} reveal some added limitations of the conventional Bridgman configuration. Using interface demarcation in Ga doped Ge these workers observed the growth rate to be transient at all times regardless of furnace configuration. The transient behavior was separated into two regimes. First, an initial transient, which obeyed a first order exponential lasting approximately 1000 seconds. Followed by a "configurational" transient, persisting for the entire growth run, and profoundly affected
by thermocouple location and/or seed cooling. The microscopic growth rate was found to deviate by as much as 25% of the lowering rate. These deviations were attributed to changes in the coupling between the charge and the furnace as a function of position. The axial gradient and interface location were found to vary as a function of crystal length. With the thermocouple located near the bottom of the furnace, (i.e. closest to the interface) these effects were minimized, since the controller adjusted furnace power compensating for changes in heat transfer. These experiments exemplified the difficulty in predicting the behavior of furnaces of classical design, and suggested the design of a system which would conform to the boundary conditions assumed in modeling.

Jasinski, Rohsenow, and Witt developed an analytical model for the axial temperature profile in a vertical Bridgman/Stockbarger furnace system. This work introduces an expression for an 'infinite length', which defines the minimum length required to eliminate thermal end effects. When the charge has infinite lengths in each isothermal zone, the interface position (i.e. heat transfer) remains constant. This implies that for constant lowering rate, the growth rate is constant and equal to the lowering rate. The model also incorporates the effects of the containment ampule, the radial gradients in the charge, and the velocity of the charge. Jasinski's analytical approach was found to yield results similar to those obtained numerically by Fu and Wilcox. Since the analytical model was easily implemented, it was used extensively in the present study to help characterize the growth conditions experienced by the charge.

In another paper Jasinski et. al. analyze the influence of various growth parameters on the radial temperature variation in the charge. The 'interface effect' is discussed and found to severely limit the ability to
influence the interface shape by position in the gradient (i.e. insulating) zone. The limitation is due to the fact that at the interface the charge undergoes a discontinuous change in thermal conductivity, while the ampule does not. For materials in which the thermal conductivity of the solid is less than that for the liquid, true for most semiconductors, the effect leads to heat transfer from the charge to the ampule in the vicinity of the interface. For semiconductors therefore, one expects the interface effect to lead to a concave interface. In the absence of latent heat effects, negligible for the slow growth rates employed in Bridgman/Stockbarger growth, the radial gradient was shown to be dependent on the gradient in the liquid, the conductivity ratio : melt/solid, and a function F. The function F is itself a function of the thermal conductivity ratio of the crucible to the solid charge, the conductivity ratio of the melt to the solid charge, and the ratio of the outer diameter of the ampule to the charge diameter.

Using finite element analysis Jasinski and Witt examined various techniques which may yield controllable interface morphology. Several methods of compensating for the interface effect were examined, including, adjustment of the axial interface position, localized heating of the ampule near the interface position, and removal of heat via the Peltier effect. The results indicate that adjustment of the interface position alone cannot overcome the adverse effects of the interface effect. Localized heating near the axial location of the interface was found to be able to invert the interface, as was Peltier cooling under low axial gradients. Methods of minimizing the interface effect which are discussed include decreasing the ampule thickness, and conductivity. Unfortunately, there are limits to this approach relating to materials properties of the containment.
In her thesis Wang describes a new furnace designed to meet the boundary conditions assumed in the aforementioned models. Specifically, heatpipes were used to provide radially symmetric isothermal zones. Growth rate experiments, utilizing coded interface demarcation in Ga doped Ge, confirmed that the growth rate was equal to the lowering rate. Growth rate transient behavior also was found to be predictable by theory. Interface morphologies for crystals grown in BN crucibles were all concave as predicted by theory. Crystals grown in quartz crucibles exhibited convex interfaces which was not expected. However, if one considers the radiation through the quartz, which is not considered in the theory, the discrepancy can be understood. Infinite lengths predicted by Jasinski's model (i.e. ~7.3 cm) were found to be very conservative, as compared to the experimentally determined values (i.e. 4.4 cm). Theoretical thermal profiles, generated by the analytical expressions and by numerical analysis, were found to agree well with those experimentally observed. These results illustrate the benefits of designing a furnace with well defined and controllable boundary conditions.

2.5 Summary

This will serve to emphasize a number of findings and conclusions which may be made based on the results presented in the previous sections.

- The electrical behavior of CdTe can be influenced by the stoichiometry of the material, and by impurities. This conclusion is based on annealing studies. To date, very little data is available on the electrical properties of as grown material which has incorporated stoichiometry control.
- Dislocation formation may be due to major deviation in stoichiometry. Dislocations may also be formed due to thermal stresses resulting from nonlinear thermal gradients or ampule wetting and differential contraction.

- The precipitate structure is expected to be affected by stoichiometric deviations. Inclusion formation has been linked to excessive growth rates. No definitive identification of the precipitates present in CdTe exists.

- Polycrystalline breakdown and the formation of twins have been linked to stoichiometric deviations, and excessive growth rates.

- Axial gradients of less than 20°C/cm are apparently detrimental to propagation of single crystals, leading to polycrystalline breakdown and twin formation.

- Of the available bulk growth techniques, the most favorable results in terms of size of crystallites has been the Bridgman/Stockbarger technique. A study which incorporates stoichiometry control and heat transfer control has not been conducted as of yet.

- Conventional furnace design does not provide adequate control of the heat transfer resulting in ill-defined growth conditions. One method of providing controlled heat transfer is by utilizing two isothermal zones separated by an adiabatic region.
Chapter 3

Approach and Structure
Given the proposed objective of this work, i.e. to examine the effect of process parameters on the properties of CdTe, these issues must be addressed.

1. Identification of the pertinent process parameters:

2. Development and implementation of methods to control these parameters:

3. Evaluation of experiments designed to resolve the contribution of the parameter in question to the materials properties:

Based on the defects observed, and their suspected causes, a number of process variables were identified. They are as follows:

- Microscopic growth rate
- Axial temperature gradient
- Radial temperature gradient
- Growth orientation
- Stoichiometry at the melt-solid interface
- Impurity content
- Wetting of containment

These variables are not directly adjustable by the researcher. Instead they can only be influenced by control or adjustment of the following parameters.

- Temperatures of furnace zones
- Dimensions of furnace components
- Ampule lowering rate
- Ampule rotation rate
- Seed crystal orientation
- Starting material purity
- Ampule material

In order to evaluate the effect of any of these growth parameters, the others must be controlled. To achieve this end, the furnace which is used to conduct the research must be able to control many simultaneous parameters. Much of the previous work has been unable to realize simultaneous parameter control due to inadequate furnace sophistication.

The first phase of the research was therefore to design a furnace which could provide a well defined thermal environment and composition control. Details regarding furnace design and its characterization are presented in chapter 4. Once a suitable furnace was available experimental techniques to purify the starting material, ampules, and characterize the as grown crystals were developed. Chapter 5 describes the experimental methods used for the present study. Results obtained during this research are presented in chapter 6. Chapter 7 contains analysis and conclusions based on the observed behavior of CdTe, while suggestions for future work are found in chapter 8. Detailed discussion of the procedures used in this study are, in general, included in the appendices. The chapters are intended to be self contained, allowing useful insight to be obtained even when reading only the chapters of interest.
Chapter 4

Furnace Design
Figure 4.1: The 'Phoenix' furnace system
Based on the previous work which has been summarized in chapter 2, a number of furnace design criteria were established.

- Well defined thermal boundary conditions to facilitate computer modeling of the system, and to allow analogies to be drawn from previous and future work

- Dimensions which would allow infinite lengths of material to extend into both the heater and cooler, thereby eliminating thermal end effects

- Precise and independent temperature control for all active zones:

- Incorporation of a third active zone to allow precise control of the vapor pressure over the melt

- Ampule alignability to close tolerance with the furnace, allowing the use of long ampules in close proximity to the furnace walls

- Completely automated operation to allow precise control of the thermal history of each crystal

- Mechanical stability enabling eventual space shuttle launch

- Modular design accommodating major changes in furnace characteristic with minimal effort

- Ease of use allowing the operator the ability to grow crystals without intimate knowledge of the system

The following chapter will briefly discuss the rational used to design the system, and introduce any pertinent methodology employed. Since much of the driving force for these designs
was based on the earlier work, it is suggested that the reader peruse the summary of these works in section 2.4. This chapter will not repeat the material summarized in the previous review section. It will however discuss the implementation employed in the present study.

4.1 Heat Transfer Control

It has been suggested that the optimum interface morphology is slightly convex. Also well known is the importance of a constant and controllable microscopic growth rate. Both these desired behaviors confirm the need for heat transfer control. The design of Wang²¹ based on two heat pipes, which act as isothermal zones, separated by an insulating zone, has been shown to provide well defined and understandable heat transfer control. However, a direct application of this design to the present study was prohibited by two factors.

1. The melting point of CdTe requires a hot zone temperature which exceeds the maximum operating temperature of present day heat pipe technology.

2. The incorporation of a reservoir zone, for vapor pressure control, exacerbates the already difficult ampule alignment procedure.

While preservation of the basic design concept was desired, i.e. dual isothermal zones separated by an insulating zone, the actual design clearly had to be changed. With this approach, the extensive data base collected by Wang, and the extensive modeling conducted by others could be utilized in the present study.
4.1.1 Furnace dimensions

The overall dimensions of the furnace components were determined by applying the infinite length criterion described by Jasinski et. al.\textsuperscript{6} The details of this procedure will be discussed in appendix D. The calculated infinite lengths for the heater and the cooler were summed with the gradient zone length to give the minimum charge length. The desired length of crystal was then added to the minimum charge length. This assures that a portion of the crystal, of the desired length, does not experience configurational transients in heat transfer. The approach is conservative since it does not consider the effect of quartz plugs which are used to seal the ampule. The plugs serve to lengthen the effective charge length, therefore the amount of crystal grown without end effects.

4.1.2 Alignment and mechanical stability

To facilitate alignment of the ampule lengths required to allow vapor pressure control, while still allowing close tolerance with the furnace, an axial alignment system and exostructure was implemented. Figure 4.2 is a schematic of the internal structure of the furnace. The exostructure consists of a series of concentric metallic spacer rings designed to interlock with the heat pipe flanges. Of major concern during the design phase of this program, was the effect of the exostructure on the heat transfer in the critical gradient zone. In an effort to study the consequence of installing an exostructure, finite element analysis of the system was performed\textsuperscript{90}. Figure 4.3 summarizes the results of this study. As can be seen from these results, the effect of the exostructure is to increase
the linearity of the profile. Since a more linear axial thermal gradient is expected to reduce thermally induced stress, the exostructure is expected to be beneficial for crystal growth. It does however reduce the axial thermal gradient near the melt-solid interface by about 30% which may be a potential problem for some materials systems.

In addition to the exostructure, a support system utilizing 2 points of attachment was employed, figure 4.2. The major challenge in designing such an attachment scheme is accommodating the thermal expansion of the furnace. Calculations based on the published thermal expansion coefficients and the expected temperatures indicate that the expansion would be between 1.27 and 1.59 cm. Consideration of the desired function of such an attachment scheme leads to the realization that elimination of lateral motion, perpendicular to the growth axis, is the primary design goal. Restriction of vertical motion is only necessary for operation in reduced gravity. Furthermore, reduced gravity does not require elimination of vertical motion. Instead it requires a force to be applied which will mimic the gravitational field and keep the furnace together. The design chosen to address these requirements utilizes three centerless ground rods and matching sleeve bearings, figure 4.2. The rods are machined to tight tolerance with the sleeve bearings, located in the lower base plate of the furnace. The rods essentially act as cantilevers, the overall tolerance at the top of the furnace is equal to the following.
\[
\tan \alpha = \frac{t}{L_b}, \quad \sin \alpha = \frac{\delta}{L_r}
\]

Since \( \alpha \) is small the approximation \( \tan \alpha \approx \sin \alpha \) holds;

\[
\delta \approx L_r * \frac{t}{L_b}
\]

where:

- \( \alpha \) = The angle at which the support rod is tilted
- \( t \) = The tolerance of the rod to bearing fit;
- \( L_b \) = The length of the bearing surface;
- \( L_r \) = The length of the support rods;
- \( \delta \) = The tolerance at the top of the furnace;

The analysis is conservative, since in order for it to be realized the three rod-bearing sets must act in concert. For the configuration used in the present study the predicted motion is less than 0.5 mm. As is suggested by the above analysis improvements could be made by increasing the length of the bearing surface. This would be preferred over decreasing the tolerance, since the later may result in galling and ultimately failure of the bearing.

Retaining springs, located below the furnace base plate, provide a force which tends to keep the furnace together even under zero gravity conditions. The springs used in the present study were 1 inch in length and provided a force of 21 pounds/inch deflection. The extension of the rods, below the base plate, is long enough to accommodate the springs and therefore the predicted furnace expansion. Changes in furnace design, e.g. the gradient zone length, are accommodated by the use of spacing tubes. Minor modifications of the design would afford the furnace system adequate mechanical strength to withstand space shuttle launch. Figure 4.4 shows the addition of a plate which
attaches to the bottom of the support rods. For launch, bolts could be extended such that they would secure the plate to the bottom of the furnace base plate creating a rigid structure. Before operating the furnace, the bolts could be retracted thus allowing the spring loaded expansion relief previously described. The system has routinely accommodated ampules of approximately 72 cm in length with a clearance of nominally 1 mm with the furnace ID.
Figure 4.2: Schematic diagram of the 'Phoenix' furnace system interior

- 72.18 cm Top of top heatpipe
- 49.32 cm Bottom of top heatpipe
- 45.76 cm Top Ni heat leveler
- 22.90 cm Bottom Ni heat leveler
- 17.24 cm Top lower heatpipe
- 2 cm Bottom of lower heatpipe
- 0 Position of ampule support shaft in upper position

Thermal Expansion Relief Mechanism for the Axial Alignment System

- 58 -
Figure 4.3: Predicted temperature profile obtained with and without exostructure
Figure 4.4: Schematic X-section of modified furnace design
4.1.3 Design and construction of a high temperature isothermal zone

Another impediment to implementing the aforementioned furnace design was the lack of availability of an appropriate heat pipe. Examination of assumed boundary conditions used for modeling\textsuperscript{6,6} indicates that an isothermal zone must extend for at least one infinite length, in order to eliminate thermal end effects. Thermal end effects manifest themselves in the form of configurational growth rate transients\textsuperscript{20}. Although heat pipes offer the most convenient method of providing an isothermal zone, they are not the only means of achieving this goal. Another approach is to use a matched heater and heat leveler, which was selected for this study.

The choice of the material to be used as a heat leveler was based on the following criterion.

- Melting point
- Thermal conductivity
- Chemical stability at the operating temperature
- Mechanical stability at the operating temperature
- Availability
- Cost

Commercially available Ni was selected as the best material for the heat leveler. A melting point of 1453°C and high thermal conductivity, approximately 0.825 W cm\textsuperscript{-1} K\textsuperscript{-1} at 1227°C, were factors which favored the selection of this material. The flanges which were used to support the heat leveler were constructed of Inconel 600 since it has improved
mechanical properties at elevated temperature. The Ni heat leveler has been used for about two years without any problems, so chemical and mechanical stability seem not to be an issue. Ni is readily available in the form of rod and is relatively inexpensive.

Designing a heater to provide heat input such that the internal temperature profile of the furnace is isothermal, requires understanding the thermal environment of the system. Experimental temperature profiles were obtained utilizing the methods described in appendix H. A simple straight wound heater was used for the hot zone to establish a baseline. Finite element analysis, using Abaqus, was then conducted on a model of the system. Figure 4.5 indicates the dimensions used in the model. The model used the known:

- Power input to the middle zone;
- Temperatures of the top and bottom zones;
- Published thermal conductivity data for all materials present;

to calculate an expected temperature profile. The only parameter which was adjusted was the heat loss to the outside surface. A comparison between the theoretically predicted and experimentally measured temperature profile is presented in figure 4.6. With what was considered a satisfactory model, an isothermal profile was imposed on the central cavity of the furnace. The model was then used to calculate the heat input required to maintain the imposed temperature profile. As can be observed in figure 4.7, designing a heater with the required characteristics would be difficult.

Two approaches were used for the design of the heater. The first was based on 4 heater elements which used shunt resistors to control the relative heat input from each.
Figure 4.8 shows the profile calculated using the model. If however, any of the shunt resistors fail, the local increase in heater power could cause severe localized heating and failure. A more conservative design was also examined which utilized 2 windings without shunt resistors. The heat input to each side of the heat leveler was adjusted by controlling the length of windings used. Figure 4.8 contains the predicted temperature profile for this more conservative design. The calculated temperature profiles suggest the 2 element design does not produce as long an isothermal zone as that obtained using the 4 element design. It is however, a much safer design not prone to the thermal runaway which is possible using the 4 element design. Therefore, the two element configuration was the one selected for the heater. The actual profile obtained with the 2 element heater is included in figure 4.9.

The position of the hot zone control thermocouple can influence the furnace response for the present configuration. The temperature gradient at the melt-solid interface is held most nearly constant when the control thermocouple is placed near the gradient zone region. Similar behavior was observed by Wang et. al.\textsuperscript{20}. Therefore, to allow for a well defined and constant gradient at the interface, the control thermocouple was placed near the gradient zone, table 1. Since the thermodiffusivity of Ni is much less than that of a heatpipe, the amount of time required for the control thermocouple to sense a change in heater temperature is greater in Ni than in a heatpipe. The end result is greater sensitivity to the controller PID constants, the system had to be highly damped so as to avoid overshoot.

Communication between zones is more severe than for heat pipe based zones. Figure 4.10 indicates the extent of
<table>
<thead>
<tr>
<th>Type</th>
<th>Zone</th>
<th>Position cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Lower</td>
<td>14.7</td>
</tr>
<tr>
<td>Safety</td>
<td>Lower</td>
<td>15.0</td>
</tr>
<tr>
<td>Control</td>
<td>Middle</td>
<td>23.9</td>
</tr>
<tr>
<td>Safety</td>
<td>Middle</td>
<td>24.4</td>
</tr>
<tr>
<td>Monitor</td>
<td>Middle</td>
<td>30.1</td>
</tr>
<tr>
<td>Monitor</td>
<td>Middle</td>
<td>40.7</td>
</tr>
<tr>
<td>Monitor</td>
<td>Middle</td>
<td>44.7</td>
</tr>
<tr>
<td>Safety</td>
<td>Top</td>
<td>55.7</td>
</tr>
<tr>
<td>Control</td>
<td>Top</td>
<td>56.9</td>
</tr>
</tbody>
</table>

Table 1: Thermocouple positions referenced to the top of the ampule support shaft in its upper position

communication between the top zone and the middle zone. The magnitude of the temperature fluctuation recorded by the monitor thermocouples is damped and decreases as they approach the control thermocouple. The 50°C top zone temperature changes result in ~10°C fluctuations near the top of the middle zone, 20.8 cm above the control thermocouple. The fluctuations are reduced to approximately 0.8°C 6.2 cm above the control thermocouple. Communication with the lower zone is not a problem since the control thermocouple compensates for changes by adjusting heater power. Installation of a separate actively controlled heating element near the top of the middle zone would afford similar isolation from top zone fluctuations. Another advantage of such a design would be more complete control of the temperature profile of the middle zone. For the present study however, the damping characteristic of the present
configuration was adequate, as will be discussed in later section.

Since the middle zone design was based on a specific set of boundary conditions, namely \( T_{1.1} = 800^\circ C \) and \( T_{1.0} = 1000^\circ C \), the internal profile is expected to change as a function of boundary conditions. For the experiments conducted in the present study, the top zone temperature was varied to control vapor pressure. Figure 4.11 presents the results of a sensitivity analysis of the temperature profile on the top reservoir temperature. The upper portion of the middle zone is strongly affected by variation in the top zone temperature. An expanded view of the region closest to the growth interface shows that the general characteristics of the heat leveler are not strongly affected by the change in boundary conditions. These results indicate that to compensate for a 250°C variation in top zone temperature, the set point of the middle zone must be adjusted approximately 7°C. Furthermore, the usual changes in top zone temperature are only 50°C, not 250°C, which reduce the influence of this effect.
Figure 4.5: Finite element grid used for calculations
Figure 4.6: Comparison of calculated and actual temperature profiles.

Distance from the Lower Heat Leveler Flange (inches)

- Calculated
- Measured

Celsius

- 67 -
Figure 4.7: Heat input required to maintain an isothermal temperature profile in the central furnace cavity.
Figure 4.8: Comparison of the predicted profiles for two heater designs

**Calculated Temperature Profile**
for 4 Element Heater Design

**Calculated Temperature Profile**
for 2 Element Heater Design
Figure 4.9: Temperature profile obtained using a 2 element heater
Figure 4.10: Damping of interzone communication

Thermal History for Hot Zone and Reservoir Zone
As Recorded by Control Thermocouples

Thermal History for Hot Zone
As Recorded by Monitor Thermocouples

Distance from control TC
- 6.2 cm
- 20.8 cm
Figure 4.11: Sensitivity of the internal temperature profile on the reservoir zone temperature

Reservoir Zone Temperature

- - - 650 C
- - - 900 C

Expanded View of Interface Region

Reservoir Temperature

- - - 650 C
- - - 900 C
4.2 Vapor Pressure Control

A reservoir zone has been incorporated in the furnace design to provide a method of controlling the stoichiometry of the crystal. By providing an isothermal zone, using a heat pipe, the partial vapor pressure of one of the components can be controlled. Since these studies were done predominantly on the binary CdTe, the vapor pressure of the two components are related by the following.

\[ \text{CdTe(s)} \rightarrow \text{Cd (g)} + \frac{1}{2} \text{Te}_2 \ (\text{g}) \]

\[ K_{\text{CdTe}} = \frac{p_{\text{Cd}} (p_{\text{Te}_2})^{1/2}}{a_{\text{CdTe}}} \]

Where:
- \( p_i \) ≡ The partial pressure of component \( i \);
- \( a_{\text{CdTe}} \) ≡ activity of \( \text{CdTe} = 1.0 \);

or \( p_{\text{Cd}} = (K_{\text{CdTe}} / p_{\text{Te}_2})^{1/2} \)

and \( p_{\text{Te}_2} = (K_{\text{CdTe}} / p_{\text{Cd}})^2 \)

Thus by controlling the vapor pressure of one of the components we can control the vapor pressure of both, and therefore the composition of the melt. In general this is not true of ternary compounds, however in the case of manganese whose vapor pressure is significantly below that of cadmium or tellurium, the above relationship is not expected to vary significantly.

4.2.1 Mass transport considerations

In the vertical Bridgman method, communication between the melt-solid interface and the vapor-melt interface requires transport through the melt for large distances. If mass transport were by diffusion alone, the effectiveness of
vapor pressure control would be minimal for the growth rates employed. For example, the nominal fluid height in the present experiments was 10 cm while the average diffusivity in liquid CdTe has been reported as $3.7 \times 10^{-3}$ cm$^2$/sec. Based on these values a characteristic diffusion time can be calculated to be of the order of $10^4$ seconds. In comparison the typical growth velocity is $5 \times 10^{-5}$ cm/sec. Clearly, no opportunity exists for diffusion to remove the rejected component from the propagating interface.

Fortunately, segregation analysis of Ga doped Ge indicates, for the furnace configuration used in this study, the behavior is very nearly that of complete mixing. In the case of severe convective mixing, communication between the vapor and solid phase is enhanced since diffusive transport is only needed in the narrow boundary layers. The nature of the convective flow pattern is not known, however numerical analyses of the system have been conducted. These analyses indicate the existence of two cells. If indeed this is the case, there are two layers in which diffusive mass transport would be expected to dominate. The classical layer associated with the solid interface, and a new layer between the two convective cells. In any event the diffusion length will be reduced considerably due to convection.

The magnitude of the convection in CdTe is expected to be different than for Ge. It is therefore of interest to estimate the relative degree of convection between these two systems. Differences between the thermophysical properties of these materials result in different Biot and Rayleigh numbers, which govern their heat transfer and convection. The results of numerical modeling are presented in figure 4.12, which compares the growth condition used for CdTe with the conditions used for the previously mentioned Ge experiments. To accelerate convergence, the model assumed a reduced gravity of 0.1 g for both systems. The exact...
<table>
<thead>
<tr>
<th></th>
<th>Ge</th>
<th>CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T</strong>&lt;sub&gt;cooler&lt;/sub&gt;, °C</td>
<td>777</td>
<td>1000</td>
</tr>
<tr>
<td><strong>T</strong>&lt;sub&gt;heater&lt;/sub&gt;, °C</td>
<td>1097</td>
<td>1150</td>
</tr>
<tr>
<td><strong>T</strong>&lt;sub&gt;melting&lt;/sub&gt;, °C</td>
<td>937</td>
<td>1092</td>
</tr>
<tr>
<td>Crystal Radius, cm</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Ampule thickness, cm</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Gradient zone length, cm</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Kinematic viscosity, cm²/sec</td>
<td>0.002</td>
<td>0.004</td>
</tr>
<tr>
<td>Density liquid, g/cm³</td>
<td>5.48</td>
<td>5.86</td>
</tr>
<tr>
<td>Thermal diffusivity, cm²/sec</td>
<td>0.20</td>
<td>0.012</td>
</tr>
<tr>
<td>Specific heat, J/(g K)</td>
<td>4.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Thermal expansion coefficient, 1/K</td>
<td>5.0 x 10⁻⁴</td>
<td>5.0 x 10⁻⁴</td>
</tr>
<tr>
<td>Thermal diffusivity, cm²/sec</td>
<td>0.09</td>
<td>0.010</td>
</tr>
<tr>
<td>Density solid, g/cm³</td>
<td>5.26</td>
<td>5.86</td>
</tr>
</tbody>
</table>

Table 2: Materials constants and furnace characteristics used for numerical modeling of fluid flow.

interface shape for CdTe could not be solved for using the present model, because it is located so close to the hot zone. Two interface shapes are therefore examined, a flat interface and an interface shape which was determined using the properties of CdTe but a lower melting point of 1041°C. Basic heat transfer considerations suggest the actual interface shape should be intermediate between these values. Both interfaces were located in the experimentally observed initial interface position. The flow magnitude reported in the figure is dimensionless, equal to:

\[(\text{flow velocity} \times \text{charge radius})/\text{kinematic viscosity}\].
Comparison of the predicted flow of Ge and CdTe indicates that CdTe experiences more vigorous flow than does Ge. Furthermore, since the location of the melt solid interface is much closer to the hot zone in CdTe than it is in Ge, the communication between these flow cells is expected to be enhanced. Another factor which enhances flow is the unstable axial temperature gradient which exists in the upper portion of the hot zone, figure 4.9. Based on these considerations it is expected that vigorous convection is present in the CdTe system which will allow communication between the melt-solid interface and the liquid-vapor interface.
Figure 4.12: Comparison of predicted fluid flow in CdTe and Ge.

Ge
Curved Interface

CdTe
Curved Interface

CdTe
Flat Interface

1 cm

0.1846

2.736

2.709

- 77 -
4.2.2 Determination of the proper P₀₆ conditions

The function of the reservoir zone is in essence to act as a source or sink of component, thus allowing growth from a liquid of constant composition. Due to the existence of a retrograde solidus (figure 2.1, and a slightly off stoichiometric congruent melting point, growth from stoichiometric proportions of starting material is expected to lead to the formation of precipitates. As a result of continued growth the concentration of reject component in the liquid continually increase therefore the composition of the solid moves toward the extrema of the solidus existence region. During cooling the solid enters a two phase region where component precipitates are anticipated. The actual type of precipitation, i.e. Cd or Te, will depend on the composition of the melt.

Assuming that we indeed have effective communication between the vapor and solid, the condensation of excess component would effectively pin the composition of the liquid. By correct selection of the liquid composition, the solid formed can be prevented from entering into a two phase region thus eliminating component precipitation. Two questions need to be answered.

1. How does the composition of the liquid change as a function of the temperature of the reservoir?

2. What liquid composition results in the formation of solid which is completely in the CdTe solid phase field, for all temperatures?

Data relating component vapor pressure to composition is not readily available. Strauss** determined that the partial vapor pressure of Cd at the congruent melting point is in
equilibrium with the vapor over pure Cd at 728°C. Detailed information on the relationship of composition and vapor pressure is not presented. Brebrick* conducts a detailed experimental determination of the partial pressures in the CdTe system and determines the solid existence region is bounded by the compositions 49.0 - 50.5 a/o Te. Combining the narrow existence region for CdTe with the vapor pressure of the congruent melting point suggests a reservoir temperature in the range about 728°C should yield material which is nearly stoichiometric.

Another approach was to apply the analytical model of regular associated solutions, first suggested by Jordan¹⁰⁰. The liquidus phase diagram for CdTe was modeled by Jordan with excellent results. The model is able to predict the liquidus curve on either side of the stoichiometric composition using only two constants, one of which, B, is a measure of the degree of dissociation of the liquid. A B value of 1.0 indicates a completely dissociated, i.e. regular, solution. The other constant, α, is related to the interchange energy and is similar to results obtained for regular solutions¹⁰¹. An important result of this work is an expression for the activity, a, of either component as a function of composition and temperature. Using the thermodynamic relation \( P_i = a_i * P^0_i \), one can calculate the partial pressure of either component \( i \) based on the vapor pressure over the pure component \( P^0 \). The details of this approach will be discussed in appendix A. Figure 4.13, contains the vapor pressure vs composition diagram which was calculated based on the above model. Caution should be used however since the model becomes less accurate near the stoichiometric composition. The data is included since it can be used to estimate the degree of departure from stoichiometry for a given reservoir temperature.
Data available for the extent of the solidus existence region is rare. The majority of the work is based on electrical measurements. Figure 2.1, contains a compilation of results for electrical measurements\(^1\). As can be seen the uncertainty in this data is high. Estimating the temperature associated with stoichiometric material from this diagram suggests that the solidus is between 20 and 25°C below the congruent melting point. The liquidus needed to yield a solid with the stoichiometric composition can be estimated using the liquidus data on the Cd rich side. Based on the data generated using Jordan's model, this corresponds to a solution of 54 a/o Cd or a reservoir temperature of \(\sim 950°C\). These approximations suggest a reservoir temperature exists between 728-950°C which will produce stoichiometric crystals. Furthermore, reservoir temperatures below 728°C are expected to result in Te rich solid.

- 80 -
Figure 4.13: Vapor pressure data

Partial Component Vapor Pressure as a Function of Composition

Vapor Pressure of Pure Components as a Function of Temperature
4.3 The Hardware

The furnace system consists of a combination of subsystems which will briefly be discussed in this section. Figure 4.14, is a schematic overview of the furnace system which has been christened the 'Phoenix'.

Three independent heaters and DC power supplies are used to provide heat input to each of the three active zones. The wire wound heaters were matched to each power supply so as to deliver close to the maximum rated power for the supply. A Kepco DC power supply providing a maximum of 1200 watts of power is used for the top, i.e. reservoir, zone. The heater used for this zone is a standard 6 inch long bifilar wound Kanthal heater purchased from ThermCraft. The middle and lower zones were powered by Electronic Measurements power supplies capable of delivering 2400 watts DC. The heater for the middle zone was a custom designed Mo wound heater which was described in section 4.1.3. The lower zone used a 4 inch long commercial Kanthal bifilar wound heater from ThermCraft. Each supply was operated in a constant current mode and was controlled by a DC signal voltage.

Temperature monitoring was achieved using inconel sheathed type K thermocouples, purchased from Industronics. The thermocouples used to obtain profiles were calibrated. The thermocouples were connected to an AIM7 board which was installed in a Keithley series 500 DAS. The resolution of the analog to digital conversion is 14 bits corresponding to a temperature resolution of ~0.03°C for type K thermocouples. Monitoring of the power to each supply was conducted by measuring the voltage across the heater input and the voltage drop across a known series resistor. These voltages were
directly input into an AIM1 board. A voltage generated by
the EGG Torque Systems 3500 series motor used for lowering
the ampules was also input into the AIM1 and served as a
method of monitoring the actual ampule lowering rate. An
auxiliary method of monitoring the lowering rate involves a
pulse generator and pulse counting circuitry which is
connected to the DIM1 board.

Safety features included in the furnace are
implemented in two ways. First, an independent hardware
based system with three separate monitoring thermocouples is
included and is capable of overriding the computer and
shutting off all power supplies. The system is based on
three independent Schmidt triggers which interrupt the power
to the power supplies if the temperature exceeds a user
specified value. Secondly, a software based protection
system monitors all the thermocouples connected to the
computer via the AIM7. It has some intelligence and will
only shut the furnace off if two thermocouples for the same
zone exceed the user specified safety limit. This feature
was included in an effort to eliminate false shutdowns
brought about by thermocouple failures. Another feature
implemented in the software and hardware is designed to
compensate for undesirable characteristics associated with
the Keithley system. When the Series 500 DAS experiences a
power interruption it goes into a state which sends full
power to all it analog output channels. This would result in
a period of time when full power would be delivered to the
heaters in the fairly likely event of a power line
interruption. For this reason a time delay circuit to the
power supplies was installed to allow the system to shut
itself off before the power supplies were activated. The
system is presently designed to shut itself off in case of a
power line interruption, but could be modified to resume
growth.
The control interface is through the AOM1/5 board, a 12 bit DA converter in the series 500 DAC. The control logic is implemented in software and will be discussed in the next section. Five analog output channels are included on the AOM1/5 board, three control the power supplies, one controls the lowering motor, and one is presently used to drive a chart recorder. The fifth output channel could be used to control ampule rotation, or magnetic field strength instead. The system is also in control of the input power to each of the power supplies. The system incorporates 3 high current relays which are activated by means of a digital signal generated by the D101 board.
**Figure 4.14: Schematic overview of the 'Phoenix' furnace system**

The temperature control algorithm and emergency shutdown logic are implemented in software. Growth run data is stored in memory then periodically dumped to a hard disk.

**Schematic Overview of the Phoenix Furnace System**

- **Inputs**
  - Thermocouple Inputs Control and Monitor
  - Power Monitoring and Lowering Rate Monitoring

- **Outputs**
  - Lowering Motor Control Signal
  - DC power supplies
    - Zone
      - Top
      - Mid
      - Low
  - Plotter
  - "Watchdog" Hardware Based Emergency Shutoff

- **Emergency Shutoff System**
- **Atmosphere Control System**

**Motor Controller**
- Rotation Motor
- Lowering Motor
4.4 The Software

In conjunction with the hardware development, a software based process control program was written. The capabilities of the software system are as follows.

- Independent definition of setpoints for three zones
- Control of the rate of temperature increase and decrease
- User definable initiation of setpoint changes
- Automated initiation of ampule lowering and control of magnitude
- Ability to superimpose growth rate pulses of adjustable magnitude and duration
- Discrete monitoring, of adjustable period, of thermocouple temperatures, heater power, and lowering rate data throughout the run

In the interest of brevity a detailed discussion of the implementation is omitted, the program is however included in the appendices. A discussion of the PID and ramp control algorithms follows.

In order to determine the optimum PID constants, a series of experiments were conducted to evaluate the open loop response for each zone. In these experiments, the signal power to each power supply was incremented and the time temperature response was recorded. After a period of time, nominally 8000 seconds, the signal was incrementally increased and the behavior again recorded. Figure 4.15, depicts the results obtained for the middle zone. These
experiments verified that the furnace could be modeled as a first order system. By fitting a first order system response to the experimental data, the furnace time constant and system resistance (actually °C/signal voltage) were determined. The signal voltage was used instead of the power to calculate the system resistance since the power supplies are controlled directly by a control voltage. In the case of Kanthol, the resistivity of the windings only changes about 1.5% so control signal is nearly equivalent to input power. For the case of Mo, the resistivity is not constant with temperature, however, figure 4.16 indicates that the steady state temperature is a linear function of input signal, which confirms that it can be used to calculate system resistance.

Comparison of the characteristic furnace time constants for each zone, nominally 3000 seconds, with the sampling period, 20 seconds, justifies a continuous-time approximation. The details of the system model, and the method used to calculate the PID constants will be discussed in appendix B. Briefly, the open loop time constant, the system resistance, the desired system damping, and desired settling time are used to calculate the proportional, integral, and derivative time constants. Some modifications, i.e. improvements, were implemented which exploit the intelligence available with a software based control algorithm to eliminate some of the shortcomings of a PID controller. A detailed discussion will be omitted however, examination of the control program should clarify these features.

While the PID algorithm was able to maintain a constant temperature to within ~0.1°C, it was not able to ramp smoothly to temperature. Part of the problem may have been due to digitization noise which was present on the thermocouple inputs. In spite of the incorporation of a smoothing algorithm, used for all control thermocouples, the
range of magnitudes available for the derivative constant was reduced. Unfortunately it is the derivative constant that generally allows a PID algorithm to track a ramp without significant lag time. To accommodate ramps, a feed forward algorithm was developed from first principles. The algorithm uses the modeled first order system response to predict the temperature which will be achieved by the addition of a given amount of power. The algorithm also uses feedback to adjusting the desired temperature change. A detailed description of the derivation and implementation is presented in appendix C.

The ramps produced using this algorithm are extremely linear, figure 4.17, gradually increasing the power to each zone. When the system is within a user specified fraction of the setpoint (FSP), it switches control to the PID algorithm. The transition is smooth but could be improved by adjusting the FSP. The worst case overshoot, for the heat leveler, is about 8°C for a setpoint of 1130°C, figure 4.18. The system comes to within 0.5°C of setpoint within about 30 minutes. The behavior of the heatpipe based zones is significantly better resulting in an overshoot of about 2°C. When setpoint is achieved, the system can control temperature to within ±0.1°C, which was the design goal. Another use of the ramping algorithm is to allow controlled temperature reduction for gradient freeze experiments. Although not investigated in this study the algorithm may be extended to allow tracking of a user defined temperature history, e.g. parabolic, logarithmic, etc.
Figure 4.15: Open loop system response for a step change in signal voltage to the power supply
Figure 4.16: Steady state temperature as a function of signal voltage

- Based on Limited Data
Figure 4.17: Typical furnace behavior

Typical Behavior of the Furnace System During a Ramp to Set-Point Temperature

Control Thermocouple for Middle Zone Typical Stability
Figure 4.18: Typically observed set-point overshoot

Heat Leveler Based Furnace Zone
Typical Overshoot

Heatpipe Based Furnace Zone
Typical Overshoot
4.5 Results

4.5.1 Interface position

Temperature profiles, figure 4.19, obtained in a model charge and the evacuated bicylindrical thermal probe (EBTP see figure H.1) confirm that the heat leveler heater combination used provides an isothermal zone (i.e. ± 2°C) which extends at least one infinite length. This suggests that the furnace still meets the boundary conditions assumed in the models. Evidence which tends to support this contention is included in table 3. The table compares the observed initial meltback interface as revealed by etching with the predicted interface using Jasinski's heat transfer model. The inputs to the model where the setpoint temperatures of the hot and cold zones, the effective gradient zone length, and the appropriate thermophysical parameters.

An effective gradient zone length was used since the model assumes that the isothermal zones extend to the edge of the gradient zone. This is not actually the case since there are end effects associated with heatpipes, and heat levelers. The end effects for heat levelers are expected to be more severe than that for heatpipes, which are nominally 1 radius. The effective gradient zone length was determined using a temperature profile obtained in the EBTP. Figure 4.19 shows that the lower heatpipe acts as an isothermal zone below 17 cm, referenced to the ampule support shaft in its uppermost position. The Ni heat leveler began to act isothermally above 25 cm. The effective gradient zone length used in my calculations was the difference, i.e. 8 cm.
Table 3: Comparison of calculated and experimentally determined interface position

<table>
<thead>
<tr>
<th>Hot Zone Temperature °C</th>
<th>Cooler Temperature °C</th>
<th>Calculated Position cm</th>
<th>Measured Position cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>1000</td>
<td>21.6</td>
<td>22.2</td>
</tr>
<tr>
<td>1150</td>
<td>1000</td>
<td>21.6</td>
<td>21.6</td>
</tr>
<tr>
<td>1130</td>
<td>1000</td>
<td>22.6</td>
<td>22.7</td>
</tr>
<tr>
<td>1130</td>
<td>1000</td>
<td>22.6</td>
<td>22.8</td>
</tr>
<tr>
<td>1130</td>
<td>1000</td>
<td>22.6</td>
<td>22.8</td>
</tr>
<tr>
<td>1180</td>
<td>1050</td>
<td>18.9</td>
<td>18.8</td>
</tr>
</tbody>
</table>

centered around 21 cm. The difference between the geometric center of the gradient zone, which is located at 20.1 cm, and the effective gradient zone center is due to the more severe end effects in the heat leveler. The geometric length of the gradient zone for these experiments was 5.57 cm indicating the total end effects accounted for approximately 2.4 cm of effective length, or about one diameter.

The agreement between the observed initial interface position, and the calculated interface position is quite good. The difference between the calculated and measured interface position is generally less than 2 mm, for a wide range of operating conditions. Furthermore, the stability of the system is remarkable with the shift in initial interface position for the same set of furnace conditions being less than 1 mm. The tolerance on the measured values is approximately ±1 mm meaning the initial interface position is reproducible within the measurement accuracy. For higher gradients, a gradient zone was used, which resulted in
isothermal behavior below 15 cm and above 22 cm for an effective gradient zone length of 7 cm centered at 18.5 cm. The predicted interface location was 19.7 cm while the observed interface occurred reproducibly at 19.8 cm. Again excellent agreement between the model and the observed behavior exists, this strongly suggests that the furnace is providing the assumed boundary conditions. Interface demarcation experiments conducted by Matthiesen\textsuperscript{103} in the new furnace have shown that quasi steady state growth occurs for Ga doped Ge. Since the Biot number for Ge is much smaller than for CdTe, it is expected that quasi steady state growth of CdTe will also occur.
Figure 4.19: Temperature profiles obtained using the evacuated bicylindrical thermal probe and a model charge.
4.5.2 Interface curvature

The interface curvature is reflective of the heat transfer in the furnace. The addition of the insulating gradient zone is expected to reduce the radial heat transfer and thus the interface curvature. In an effort to determine the interface curvature, a series of experiments were conducted which used etching and infrared macroscopy to demarcate the interface. The etching experiments revealed the initial meltback interface as is shown in figure 4.20. The interface appears planar to within the resolution of the technique. However, this interface shape reflects a static configuration, no charge movement for nominally 3 hours before lowering begins.

Attempts at dynamic demarcation of the interface have not been possible to date. The methods which were employed in the present study to demarcate the interface were all based on enhanced segregation due to growth rate increase \(10^4\). Both growth rate pulsing and step changes in growth rate were conducted without success. Ag was used as a dopant since it produces a broad band absorption in the infrared, figure 6.1, and has a segregation coefficient \(10^5\) \((k)\) of approximately 0.009. In doping was also attempted since it contributes free electrons to the lattice and should result in free carrier absorption, \(k \approx 0.11\). The initial concentration of Ag was \(\sim 10^{19}/\text{cm}^3\) while that for In was \(\sim 10^{20}/\text{cm}^3\).

The pulsing experiments consisted of changing the lowering rate from 0.2 cm/hr to 2.0 cm/hr the duration of the pulse was 1800 seconds repeated every 18000 seconds. For the In doped material infrared microscopy did not indicate any change in absorption due to the pulse. The sample appeared uniformly transparent in the near IR, however spectra were
not obtained to quantify this impression. A similar lack of any demarcation events characterized the Ag doped experiment.

Since a system lag to growth rate change was suspected, a step change in growth rate was also attempted. The growth rate was changed from 0.2 to 2.0 cm/hr. In figure 4.21, a faint line which corresponds to the time at which the growth rate was changed, can be seen. The image was produced by imaging the crystal with a Si vidicon which is sensitive to the near IR. The uneven illumination is due, in part, to the illumination system of the apparatus and in part to a grain boundary which is labeled. FTIR was used to measure the absorbance of the sample as a function of position along the axial direction. Figure 4.22, indicates a change in slope which corresponds to the position of the growth rate change. The slope of the absorbance curve increases at approximately 40 mm which is where the growth rate was increased. The notch in absorbance between 45 and 48 mm corresponds to the grain boundary.
Figure 4.20: Initial meltback interface shape
Figure 4.21: IR macroscopy of Ag doped CdTe experiencing an increase in growth rate from 0.2 cm/hr to 2.0 cm/hr
Figure 4.22: FTIR analysis of Ag doped CdTe which has experienced a growth rate change from 0.2 cm/hr to 2.0 cm/hr.
<table>
<thead>
<tr>
<th>Hot Zone Temperature °C</th>
<th>Cooler Temperature °C</th>
<th>Effective Gradient Zone cm</th>
<th>Calculated Relocation Length cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>1000</td>
<td>8</td>
<td>&lt; ± 2 μm</td>
</tr>
<tr>
<td>1130</td>
<td>1000</td>
<td>8</td>
<td>&lt; ± 2 μm</td>
</tr>
<tr>
<td>1180</td>
<td>1050</td>
<td>8</td>
<td>&lt; ± 2 μm</td>
</tr>
<tr>
<td>1150</td>
<td>900</td>
<td>7</td>
<td>&lt; ± 55 μm</td>
</tr>
<tr>
<td>1130</td>
<td>900</td>
<td>7</td>
<td>&lt; ± 55 μm</td>
</tr>
</tbody>
</table>

Table 4: Predicted interface relocation due to a ± 0.8°C Hot Zone Fluctuation

4.5.3 Sensitivity of interface position to fluctuations in reservoir zone temperature

It has been shown previously that the hot zone communicates with the reservoir zone. In an effort to estimate the effect of these changes Jasinski's heat transfer model was used to calculate the interface position for a variety of boundary conditions. The boundary conditions reflected the various growth configurations used and the experimentally determined fluctuations due to reservoir temperature changes. Table 4 summarizes these findings.

The temperature fluctuations of 0.8°C, which were observed 6.2 cm above the control thermocouple, occurred over a period of about 3000 seconds. By using the above predicted interface relocation an effective growth rate can be determined. For the most severe relocation of 55 μm the effective growth rate is ~2 A/sec which is much less than the
growth rates used ~60 A/sec. The analysis is conservative since the infinite thermal length for CdTe is ~4 cm which would correspond to even smaller fluctuations in hot zone temperature.
Chapter 5

Experimental Procedure
5.1 Crystal Growth Methods

Crystal growth processing is a complex activity which requires successful completion of a critical series of procedures before yielding a result. These procedures include purification of materials, ampule preparation, control of composition, and control of growth parameters. The following section briefly describes the procedures followed in the present study.

5.1.1 Material purification and charge preparation

The Cadmium Telluride used in this study was synthesized from commercially purchased 6N Cd and 6N Te from Johnson Matthey. Initially both Cd and Te were further purified by sublimation, however after a number of experiments it was discovered that sublimation of Te did not noticeably improve its purity and this procedure was terminated. The sublimation of Cd did lead to separation of a greenish brown flaky residue. Spectrochemical analysis of the residue revealed its composition to be predominantly Cd suggesting that it was an oxide. Other elements detected were Pb, Mg, Si, Cu, Ag, Al, Bi, Fe, Mn, Na, Zn, Ca, Ti, and possibly Ni. Sublimation was carried out in quartz tubes which had been cleaned in PEX, a laboratory glass cleaner; Aqua Regia; HF; and thoroughly rinsed in deionized H₂O after each step. The final cleaning step included a vacuum bake at 1000°C, and ~5x10⁻⁷ torr for a period of not less than 12 hours, and generally considerably longer. The internal surface of the ampule was coated with pyrolytic graphite to prevent reaction between the Cd and the quartz. Graphite coatings were deposited by pyrolysis of acetone in precleaned ampules. After the coating was applied the Vacuum bake
procedure was repeated. Sublimation was carried out at ~ 450°C, the purified Cd was sealed in the ampule and stored until it was needed.

Another ampule was prepared for reaction of the elements using the aforementioned cleaning procedure. In general this ampule was graphite coated to minimize the potential for reaction of the elements with the quartz. Equimolar quantities of purified Cd and Te were weighed out and placed into the ampule. The ampule was then evacuated and purged with Ar gas, finally being evacuated to better than ~5x10⁻⁷ torr. After sealing the reaction was initiated by placing the ampule into a furnace operating at nominally 800°C. The reaction was generally allowed to proceed for about 8–10 hours. It was discovered that the free volume, i.e. portion which did not contain charge material, in the ampule was an important parameter. If there was not enough free volume, the reaction would not proceed to its completion, and pockets of elemental Cd and Te could be observed. Empirically it was determined that about 50% free volume was needed to allow complete reaction. The ampule was then placed into a simple Bridgman furnace, melted, then lowered at a relatively rapid rate ~ 3 cm/hr, to ensure complete reaction. In a few cases when the ampule was not coated, a white powder was visible on the surface of the crystal after the reaction was completed. The material produced by this method was either used directly or cast into a suitable shape for growth. When used, 6N commercially purchased Mn was added, no additional purification steps were incorporated. The doping elements In and Ag were also used as purchased with no additional purification procedures.
5.1.2 Ampule design and preparation

The Ampules used to grow crystals were specially designed to permit vapor pressure control (VPC) over the melt. In order to achieve VPC the ampules had to be long enough to ensure that a portion of the ampule was kept in the isothermal reservoir zone at all times. Figure 5.1 shows the important features of the ampule. The dimensions are nominally:

- Bottom seal - 22 cm from the ampule base
- Condensation collecting aperture - 50 cm
- Top of ampule - 71 cm

For experiments not involving rotation the ampules used were nominally 20 mm OD and 16mm ID. When rotation was employed the ampules used were 19 mm OD and 15 mm ID. The reduction in ampule diameter was necessary to ensure that the ampules did not strike the furnace wall while rotating. Attachment to the lowering shaft was achieved using stainless steel set screws as shown in the figure 5.2. This design assured no slippage during lowering and rotation. All Ampules were cleaned using the procedure described in the previous section 5.1.1. When graphite coatings were used they were prepared as described in the aforementioned section. All charges were evacuated to better than 5x10^{-7} after back filling with Ar then sealed.
Figure 5.1: Ampule Design for VPC CdTe Growth

Schematic Diagram of Growth Ampule

Reservoir Region for Vapor Pressure Control

Condensation Collector

Charge Material

Seed Crystal

Bottom Seal

Quartz Pedestal Used to Position Seed

Nominal 16mm ID by 20mm OD
Figure 5.2: Ampule Attachment Mechanism

Each Section is attached via Stainless Steel Set Screws

Coupling

Ampule

Ampule Support Shaft
5.1.3 Seeding and necking

The effect of crystallographic orientation on the growth behavior of CdTe was examined by seeding in the following orientations, [100], [110], [111]B. Seeds were obtained thanks to Dr. Piotr Becla of MIT, Dr. Don Hobgood of Westinghouse, Dr. Luigi Colombo and Ms. Bobby Baird of Texas Instruments. In all cases successful seeding was confirmed by examining the orientation of the first to freeze portion of the crystal.

In most cases seeds were of a smaller diameter than the ampule, necessitating the use of seed holders. In general the thermophysical properties of the seed holder are different than those for CdTe, complicating the seeding procedure. The materials used as seed holders were boron nitride and quartz. These materials were chosen because they are suitable refractories with thermophysical properties similar to those of CdTe. Graphite was not used as a seed holder since its thermal conductivity is much higher than that of CdTe.

In all cases accurate interface position is needed to ensure that the seed will be partially melted back but still remain intact. The interface position was initially determined empirically by examining the melt back position of a precast charge by means of a differential etch (figure 4.20). Combining the measured interface position, temperature profiles obtained using the same furnace conditions, and the analytical axial heat transfer model developed by Jasinski\textsuperscript{44}, the interface position was determined for other furnace conditions. Comparison of the experimentally determined position to that predicted by the model yields good agreement, see table 3. Reproducibility of
the interface position for a given set of furnace conditions was usually better than ± 1 mm.

Experiments were conducted to examine the effectiveness of conical ampule bottoms, long narrow tubes at the ampule end, and diameter constrictions for enhancing grain selection. The constrictions were made of the following materials, quartz, boron nitride, and graphite. Graphite was used in this set of experiments since it was felt that the wetting behavior of the material was more important than the thermal properties. This is because for the case of a constriction, the interface position need not be predictable for the success of the experiment, so long as it does not stepwise relocate. Three configurations were examined.

1. The charge below the constriction was completely melted.

2. Some CdTe powder remains in solid form below the constriction. The initial melt-solid interface is adjusted to be below the constriction.

3. An oriented single crystal is placed below the constriction and partially melted back.

5.1.4 Vapor pressure control

The crystal growth experiments always employed some form of vapor pressure control. In general this meant that the top heatpipe was kept at a constant temperature while the charge was lowered. In most crystals the Cd vapor pressure was controlled, this was necessitated by the composition examined in the experiments. The vapor pressures of Cd over CdTe were obtained from the literature\textsuperscript{28}. Two methods were employed for composition control. In the first stoichiometric
CdTe produced as in section 5.1.1 was lowered with a reservoir temperature which was determined to force vapor transport of Cd from the melt. After a portion of the crystal was grown under these Te rich conditions the temperature of the reservoir was adjusted to yield near stoichiometric growth. This behavior was confirmed by the observation of Cd metal which had been rejected from the melt to the top zone. In a second approach a small quantity of excess Cd was added to the top section of the ampule and the temperature of the top zone was adjusted to give the desired growth conditions. In general the former approach is simpler and satisfactory for near stoichiometric growth, however, the first to freeze portion of these crystals are necessarily Te rich. The latter approach is useful throughout the near stoichiometric compositional range.

Effective control of the composition of the solid by VPC requires rapid equilibrium of the vapor with the melt at the melt solid interface. This requirement necessitates rapid fluid flow. This may be brought about by natural or forced convection in the melt. Experiments were conducted examining the effect of rotation of the ampule on the materials properties.

5.2 Materials Characterization Techniques

Materials characterization requires, in general, specialized specimen preparation. The following section will briefly outline the techniques used in this study, the information which can potentially be obtained, and any special specimen preparation required. Any in-depth explanations will be delegated to the appendices or the references.
5.2.1 Chemical etching

Chemical etching was used in conjunction with optical microscopy and macro photography to reveal grain boundaries, twins, etch pits, and growth striations. Etches identified during a literature review were tried, with mixed success. In particular Nakagawa's\textsuperscript{107} etch did not consistently show etch pits. It was used however to differentiate (111)A from (111)B faces. The etches described by Inoue\textsuperscript{108} et al yielded more consistent etch pit formation. The differential etching characteristics of the etch were shown to be due to the addition of the Ag\textsuperscript{+} ion which replaces Cd in the etching reaction. The Inoue etch has been widely used in the literature\textsuperscript{109,110}, however there has been some doubt raised as to whether it actually reveals dislocations\textsuperscript{107}. There has not been any direct correlation of the etch pits produced by the Inoue etch and dislocations, rather the etch pit density has agreed with dislocation densities determined using TEM\textsuperscript{110}.

The etch that was routinely used in this study was by volume 1 HF : 3 HNO\textsubscript{3} : 4 2\% Aqueous AgNO\textsubscript{3}. It had been reported as a grain boundary and twin boundary revealing etch\textsuperscript{111,115}. As can be seen in figure 5.3 the etch can be used to reveal striations in CdTe. Furthermore, figure 5.4 shows a correspondence between the decorated dislocations and etch pits. Thru-focus experiments conducted on this sample confirm that the decorated dislocations seen in IR microscopy terminate in etch pits. The dislocations networks produced by the etch, labeled N in figure 5.2.1, are also shown to correlate well with those revealed by x-ray topography, figure 5.6. The etch was also used to reveal the initial liquid solid interface position as shown in figure 4.20.
Figure 5.3: Striations in LEC CdMnTe revealed by etching
Figure 5.4: Decorated dislocations terminating at etch pits
Figure 5.5: Montage of dislocation networks revealed by etching
Figure 5.6: Montage of networks revealed by X-ray topography
5.2.2 Infrared microscopy

IR microscopy was found to be useful in obtaining information relating to precipitate or inclusion densities, and the distribution of decorated defects such as dislocations or boundaries. The system used in this study was based on an Axiotron optical microscope, a Dage series 70 PbS or series 67M Si vidicon, and supporting electronics. Images were recorded on 1/2 inch video tape and transferred to a MassComp model 5500 computer equipped with a Polaroid video printing system model 48. The images were then transferred to 35 mm film Kodak pan-X ASA 125. The scan lines visible in the IR micrographs are therefore byproducts of the image formation process.

Specimens were prepared for IR microscopy by first cutting them with a wire saw using SiC and glycerin as an abrasive. The specimens were then mounted on a stainless steel polishing jig with crystal bond, a low temperature thermal adhesive, thereby ensuring a high degree of planarity. The samples were then polished using the following steps.

1. 600 grit SiC abrasive pads to remove saw damage and to flatten the surface of the sample

2. 0.3μm Al₂O₃ and DI H₂O, Linde A, using a Buehler Microcloth No. 40-7222 pad. This step removed the damage introduced during the previous step and yielded a mirror like surface.

3. 0.05μm Al₂O₃ and DI H₂O, Linde B, using a Buehler Microcloth No. 40-7222 pad. This step was used to eliminate the scratches sustained during the previous step.

- 118 -
4. A final chemical-mechanical polish of 125 ml Nalcoag No. 2355 and 125 ml DI H₂O with 2 ml H₂O₂, was used on a Rodel No. 204/II pad. This procedure is a modified version of the one reported by B. Fabes. It was found that the resulting polish was improved significantly by dripping a 3:1 solution of Clorox and DI H₂O. The 0.05μm scratches of the previous step were removed in this procedure.

In many cases samples which were being prepared for IR microscopy skipped the final polishing step since it was discovered the residual scratches formed useful fiducial marks demarcating the sample surfaces.

5.2.3 InfraRed spectroscopy

IR spectroscopic techniques are capable of yielding information relating to the presence of optically active defect levels, band edge energy, and free carrier concentration. The slope of the fundamental edge can give a qualitative indication as to the extent of band tailing due to shallow defect levels. In the present study, IR spectroscopic measurements were made at room and liquid nitrogen temperatures. The wavelength ranges examined included the near IR, band edge to about 2μm, and the mid IR from ~2μm to ~40μm. A method of determining Mn alloy composition as a function of spatial position was developed based on the associated shift in fundamental edge position. The technique is applicable to any alloying element that causes a shift in fundamental edge energy as a function of composition. The sample preparation technique used is the same as that used in the previous section 5.2.2. Particular care must be taken in assuring that the sample surfaces are parallel to each other, thus care must be taken when mounting the sample on the polishing jig.
A number of spectroscopic methods were employed in this study. A Cary model 17D spectrometer was used in the near IR to about 2.6μm. A Beckman Acculab 10 was used for the mid IR measurements from about 2.5 to 40μm. A Bio-Rad Digilab model FTS-60 FTIR spectrometer was used in the spectral range ~ 0.8μm to ~ 25μm, however, it was necessary to change the beam splitter to cover the entire range. The microspatial IR spectroscopy referred to in the previous paragraph was based on a Photoresearch model PR-713 fast spectral scanner mounted on a Wetzlar optical microscope. Two basic spectroscopic techniques were employed by these instruments. The Cary and the Beckman utilize two beam spectrometers. Their output is analog, recorded on chart paper. The Digilab FTIR and the Photoresearch are single beam instruments which use a temporal ratioing technique, their output is digital. Comparative studies of both types of instrument yielded no clear advantage for either. The FTIR was therefore used increasingly as my studies proceeded since the results are obtained more quickly and can be analyzed more rapidly.

5.2.4 Electrical measurements

Two types of electrical measurements were conducted, Hall effect measurements and resistivity measurements. Hall effect measurements were only conducted at room temperature for as grown undoped p-type samples. This was necessitated by the fact that the samples experienced freeze out of carriers at liquid nitrogen temperature. The electrical contacts for all Hall effect measurements were checked for ohmicity using a Tektronix transistor curve tracer type 575 prior to the measurements. Resistivity as a function of temperature was conducted to determine the freeze out behavior of the samples. A four point probe arrangement was used to minimize
any effect of contact non-ohmicity as the temperature was decreased.

The difficulty in producing low resistivity ohmic contacts on low to medium resistivity p-type CdTe is well documented\textsuperscript{113,114,115}. Most of the reported contacts involve deposition of Au onto a polished CdTe surface. The most common method to deposit Au is by electroless deposition from a AuCl\textsubscript{3} solution. The technique was first described by DeNobel\textsuperscript{19} and has been used extensively since then. Although the methods involving Au deposition were found to work, they did not produce ohmic contacts on all material. This necessitated the confirmation of the contact ohmicity by use of I-V curves. Recent work in the area of metal/CdTe interfaces suggests that such behavior may be due to exposure to air\textsuperscript{116,117,118}. With this in mind a specially designed glove box was constructed which facilitates the fabrication of electrical contacts under an inert atmosphere. For the samples where AuCl\textsubscript{3} solution did not produce ohmic contacts Li was diffused at low temperature using a modification of the method reported by Lee and Bube\textsuperscript{119}. The samples were etched in 5% Br-Methanol and rinsed in isopropanol and methanol while under an inert He atmosphere. They were then annealed while still under He at ~200°C for about two minutes then raised to 300°C for ~10 seconds. This method of production of ohmic contacts was found to yield satisfactory contacts on all the material produced in this study.

5.2.5 Electron microscopy

Electron microscopic methods used in this study include SEM-EDX, electron microprobe, TEM, and STEM. The techniques are well developed and explained in the literature\textsuperscript{120,121,122,123}. Preparation of satisfactory specimens however is not so well developed in the literature
and will be discussed. SEM and electron microprobe allow the use of bulk samples, therefore, the previously described polishing method 5.2.2 was used for these samples. TEM and STEM require the use of electron transparent specimens. This necessitated the development of specialized techniques to produce samples. Although many methods of preparing electron transparent samples were attempted, the following discussion will be limited to the most successful methods.

Successful thin film preparation was found to require orientation of the sample to the non polar [110] direction. Attempts at producing samples in other orientations could not produce adequate thin area. It is suspected that this is due to bending caused by differential stress experienced by opposite surfaces in the polar directions for these systems. The oriented wafers were polished until they were flat and mirror-like using a procedure similar to the one described earlier 5.2.2. No final chemi-mechanical etch was employed. The samples were then remounted on the opposite face and polished using the same procedure until they were approximately 200 μm thick. Discs of 3 mm diameter were then cut using a coring drill and a slurry of 5 μm garnet grit in H₂O. The discs were then chemically thinned to electron transparency using a 0.5% Br₂ in CH₃OH+C₂H₅OH solution. The equipment used for the chemical polishing was based on a modified Fischione electro-polisher, which is standard equipment for sample preparation of metals. Briefly, the critical modification involves filtering out illumination which is of energy below the band edge for the auto shutoff system. When this feature was implemented reproducible TEM samples resulted. The chemically thinned samples are apparently free of any polishing introduced artifacts. Due to the difficulty in assessing the number of dislocations before polishing, their introduction cannot be precluded. The low dislocation density observed tends to
indicate that few if any are introduced by polishing (figure 5.7a).

Ion milling was also found to be useful in preparing samples for high resolution TEM. It was discovered however that ion milling introduces artifacts which appear to be dislocation loops (figure 5.7b). A detailed investigation of these features was not made since it was beyond the scope of the proposed research. We can conclude from the present work that evaluation of the as-grown microstructure using samples prepared by ion milling is impossible. A variety of beam energies and angles of incidence were employed. The damage was minimized using shallow angles of incidence and low beam energies (i.e. 2 KeV, 0.5 mA, 15°). At very low angles of incidence, i.e. 5°, an extremely mottled surface was observed (figure 5.7c). As was expected, using a liquid nitrogen sample stage did not reduce the number of dislocation loops introduced by this technique.
Figure 5.7: TEM specimens produced using different methods.
A: Chemical Polish  B,C: Ion Milling
5.2.6 X-ray techniques

Laue back reflection was used to identify the growth orientation\textsuperscript{125,126}. A x-y eucentric translation goniometer stage was developed during the course of this study to allow the relative orientation of adjacent grains to be determined. In the course of these experiments, Laue diffraction was conducted without disturbing the goniometer tilt or sample by simply translating the adjacent grain into the X-ray beam. The relationship between the adjacent grains was determined by calculating the 24 possible axis angle pairs and selecting the minimum angle. The details of this analysis will be presented in appendix F. X-ray topography using the Berg-Barrett method\textsuperscript{127} was conducted to test the effectiveness of the dislocation etch courtesy of Dr. Colombo and Ms. Baird of Texas Instruments.
Chapter 6

Results and Discussion
6.1 Doping Effects

The effect of dopants was not systematically examined. However, some limited data was obtained and is reported here for the benefit of the interested. Ag was investigated in the course of this study. The investigation of Ag was part of an effort to demarcate the interface shape, section 4.5.2. Ag doping was found to introduce broad band absorption in the infrared. Figure 6.1 and figure 6.8 are the measured absorbance spectra for the near and mid IR for Ag doped and undoped CdTe respectively. Hall effect measurements obtained on Ag doped CdTe at room temperature conclude that the material is p-type with a hole concentration of $\approx 4 \times 10^3$/cm$^3$, mobility of $\approx 50$ cm$^2$/V-sec, and a resistivity of $\approx 3000$ $\Omega$-cm. Although Ag is known to segregate strongly, $k \approx 0.009$, the electrical measurements yield nearly identical results regardless of position in the boule. The optical absorption is a function of the Ag concentration, with absorption increasing near the last to freeze portion of the crystal. In regions of the crystal which are still transparent enough to allow IR microscopy to be conducted, a network structure of defects is observed, figure 6.2. The prevalence of the structure increases as one moves away from the first to freeze portion of the boule, i.e. increasing Ag, until the crystal is completely opaque. The absorption coefficient in the range of 0.1 to 0.5 eV and 0.4 to 1.4 eV have been fit to a power curve.

$$\alpha = b E^a$$

where:

$\alpha =$ Absorption coefficient cm$^{-1}$

$E =$ Energy eV

In the range of 0.1 to 0.5 eV
A = 2.56  b = 9.91  Correlation coefficient squared (R^2) = 0.967

In the range of 0.4 to 1.4 eV

A = 1.82  b = 5.98  R^2 = .997
Figure 6.1: Infrared spectra obtained on Ag doped CdTe
Figure 6.2: IR microscopy of Ag doped CdTe
6.2 The Effect of Growth Velocity

The criticality of the microscopic growth rate on ultimate crystal quality has long been known. The degradation in quality, due to excessive growth rates, can be related to constitutional supercooling\textsuperscript{1,2}, or to a variation in interface shape due to an increase in Peclet number\textsuperscript{3,2}. The maximum growth rate, which will yield single crystals of good quality, for a given axial gradient, is dependent on materials properties and furnace characteristics.

6.2.1 Results

The effect of growth rate was studied by increasing the lowering rate from 0.2 - 1.2 cm/hr during the growth process. The crystal was then examined using infrared microscopy. The number of precipitates in the structure increases dramatically with increasing growth rate. When the crystal is lowered at 0.2 cm/hr the IR micrograph figure 6.3A indicates virtually no precipitates are present. If the lowering rate is increased to 0.6 cm/hr the number of precipitates increases dramatically, as in figure 6.3B. Further increases in lowering rate led to precipitates of larger diameter, figure 6.3C and the beginnings of inclusion formation figure 6.3D. Increasing lowering rate will eventually lead to polycrystalline breakdown. Figure 6.4 demonstrates how a change in lowering rate from 0.2 cm/hr to 2.0 cm/hr leads to polycrystalline growth.
6.2.2 Discussion

The observed behavior of increasing precipitate density with growth rate suggests that constitutional supercooling, not interface curvature, effects eventually lead to polycrystalline breakdown. The morphology of the observed 'precipitate' structure is also typical of included material due to interface breakdown by constitutional supercooling. Jasinski et. al. contend the heat transfer due to the Peclet effect, a ratio of the axial heat transfer due to lowering velocity and due to conduction, is negligible when the following inequality holds.

\[ \text{Pe}^* / (4 \text{ (Bi}^*)^{1/2} ) << 1 \]

Where:

\( \text{Pe}^* \equiv \) An effective Peclet number which considers the effect of the crucible.

\( \text{Bi}^* \equiv \) An effective Biot number which considers both the crucible and radial gradients.

Considering the growth parameters and materials properties used in the present study the effective Peclet number was approximately two orders of magnitude lower than the effective Biot number for the highest velocities used. Using the above criterion, it is clear that charge motion effects should have only a limited effect heat transfer and therefore on the interface shape. This lends greater support to the idea that constitutional supercooling effects dominate the adverse influence of high growth velocities.
Figure 6.3: The effect of changes in growth rate on microstructure A = 0.2 cm/hr; B = 0.6 cm/hr; C = 1.2 cm/hr; D = 1.2 cm/hr
Figure 6.4: Initiation of polycrystalline growth due to a lowering rate changed from 0.2 cm/hr to 2.0 cm/hr
6.3 The Influence of Reservoir Zone Temperature

As discussed in section 2.2, the vapor pressure of component is expected to have a profound effect on the electrical properties of CdTe. This behavior has been observed in annealed material. Furthermore, it is expected that deviation from stoichiometry will cause the formation of precipitates due to the existence of a retrograde solidus on both the Cd and Te rich sides of the phase field. Increases in the density of dislocations due to deviation from stoichiometry have also been observed in compound semiconductor systems\textsuperscript{129}, thus may be expected to vary as a function of reservoir temperature. The third actively controlled zone was designed specifically to accommodate the investigation of stoichiometric effects. With this zone the component vapor pressure could be controlled during the growth process.

6.3.1 Results

The effect of vapor pressure changes were studied by characterizing material which had been produced using different reservoir zone temperatures. All crystals were produced using a lowering rate of 0.2 cm/hr. A number of experimental approaches to vapor pressure control were utilized as described in section 4.2. The crystals were grown either under a fixed setting of the reservoir zone temperature, or with changes in reservoir temperature during a given run. Characterization of the samples included IR microscopy, room temperature Hall effect measurements, resistivity v.s. temperature measurements, IR spectroscopy, and STEM.
As can be seen in figure 6.5, variation of the reservoir zone temperature had profound effects on the microstructure of the crystals produced. For a reservoir zone temperature of 800°C, a cadmium rich condition, a wispy structure can be observed. The wispy structure may however be due to impurities, since crystals produced using a reservoir temperature of 850°C do not exhibit a similar structure. Lowering the temperature of the reservoir to 750°C resulted in a structure very nearly clear of precipitation. The temperature which corresponds to stoichiometric CdTe has been reported to be 728°C. Temperature profiles of the furnace have shown that the internal cavity is actually 18°C lower than the control thermocouple or 732°C, very nearly the stoichiometric value. A reservoir temperature of 700°C led to the formation of spherical precipitates which tend to decorate dislocations. Further decrease of the reservoir temperature to 650°C results in an increase in the density of the spherical precipitates. STEM analysis, figure 6.6, of morphologically similar precipitates reveals that they are composed of elemental Te. Changing the reservoir temperature did not result in a dramatic boundary between the adjacent regions of the crystal, rather a gradual change was observed. Growth runs which had reservoir temperatures above 800°C yielded crystals which invariably exhibited metallic Cd inclusions.

The electrical and optical properties of the crystals produced for various reservoir zone temperatures did not show any major changes in behavior. Figure 6.7 shows the resistivity vs temperature behavior of samples grown with varying partial pressures of Cd. The slopes of the various curves do not vary strongly especially in view of the approximate nature of the measurement. Using the technique described by Becla et. al. a trap level was identified at 0.147 ± 0.020 eV which appears to dominate the electrical
properties. Room temperature Hall effect measurements indicate a nearly constant hole concentration for all growth conditions. The value measured at approximately $1 \times 10^{14}/\text{cm}^3$ is comparable to the lowest values reported in the literature. However, it is much higher than the predicted intrinsic carrier concentration, suggesting the electrical properties are dominated by an unintentional impurity. The optical behavior of these materials also shows no clear correlation with the component vapor pressure used during growth. Figure 6.8 shows the behavior of the absorption coefficient as a function of reservoir temperature. The major fluctuation which can be observed is a baseline shift. The baseline shift is not likely to be due to materials properties, rather it reflects instrument instabilities.

6.3.2 Discussion

The negligible influence of the reservoir temperature on the electrical and optical properties can be understood if we consider the thermal history of each growth experiment. Due to the existence of a lower heat pipe, figure 4.2, the crystal experiences an anneal at elevated temperatures, nominally 1000°C, for approximately 90 hours. Considerable evidence exists for atomic mobility at relatively low temperatures in CdTe, some of which has been discussed in section 2.2. Based on reported values\textsuperscript{31} for the self diffusion coefficients for Cd and Te, the diffusivity of Cd can be calculated to be greater than $3 \times 10^{-9} \text{ cm}^2/\text{sec}$ at 1000°C. The diffusion coefficient for Te self diffusion can be shown to be approximately $6 \times 10^{-10} \text{ cm}^2/\text{sec}$ at the same temperature. Using the familiar $x \approx \sqrt{Dt}$ we can estimate the distance the excess Cd or Te would be able to diffuse during the anneal. For Te the calculated distance is nearly 150 μm,
for Cd the diffusional distance is greater than 300 μm. These values of the diffusion coefficients do not specifically include any enhanced diffusion which may exist for dislocations and grain boundaries. If we consider a crystal with a low dislocation density of $1 \times 10^6$ cm$^{-2}$, the average separation between dislocations is approximately 100 μm. This suggests that for the annealing history experienced by the crystal, there is ample time for diffusion to heterogeneous nucleation sites. It is understandable therefore that precipitation of excess component occurs in this system. Furthermore, since precipitation removes the electrically active components from the matrix, it effectively neutralizes their influence.

For growth on the Cd rich side of the phase diagram, the interface appears to become unstable at 0.2 cm/hr for compositions which are in equilibrium with a reservoir temperature greater than 800°C. If these observations are combined with the published solidus existence region, figure 2.1, and the data presented in table 7 we would conclude the solid never reaches the stoichiometric composition always being Te rich. This conclusion is unfortunately based on inexact data and must only be used with caution. It would however explain the lack of observed precipitates for growth with reservoir temperatures above 750°C. Furthermore, it would explain the p-type electrical behavior observed regardless of reservoir temperature. Difficulties with the production of n-type CdTe by adjusting the composition of the melt have been reported in the literature$^{39}$, with n-type crystals only being produced in synthetic ampules. However, synthetic quartz ampules have significant amounts of Cl present, which is a donor in CdTe. Using lower growth rates may allow the production of n-type CdTe, since if stable growth at higher reservoir temperatures were possible Cd rich solid would be expected.
Figure 6.5: The effect of variations of reservoir zone set point
Figure 6.6: Scanning transmission electron microscopy data of a Te precipitate
Figure 6.7: Electrical properties as a function of reservoir zone temperature

Room Temperature Hall Effect Measurements
Carrier Concentration as a Function of Reservoir Temperature

Resistivity as a Function of Temperature for CdTe

- 141 -
Figure 6.8: Near and mid IR absorption coefficients

Absorption Coefficient as a Function of Energy (Near IR)

Reservoir Temperature
- 650 C
- 700 C
- 750 C
- 800 C

Energy (eV)

Absorption Coefficient as a Function of Energy (Mid IR)

Reservoir Temperature
- 650 C
- 700 C
- 750 C
- 800 C

Energy (eV)
6.4 The Effect of Ampule Rotation

As suggested in section 4.2, the ability to control the stoichiometry at the growth interface assumes rapid mass transport through the melt. For Gallium doped Germanium, experimental evidence suggests that this is indeed the case\(^2\). However, the materials properties of CdTe are significantly different than those of Germanium. In an effort to increase the fluid flow, and therefore mass transport through the melt, experiments using ampule rotation were conducted. Numerical modeling, courtesy of S. Motakef, figure 6.9, suggest that rotation at constant velocity could increase the fluid flow in the melt.

6.4.1 Results

Figure 6.10 shows a strong correlation between reservoir temperature and external crystal morphology. In this experiment no excess Cd was added to the reservoir zone. The ampule was rotated at a constant velocity of \(~17~\)RPM. The arrows in the figure indicate positions where the reservoir temperature was increased by 50°C, initially starting at 650°C for the position labeled "i". Changing the reservoir temperature to 800°C initiates the formation of external pits. InfraRed microscopy of axial slices of the crystal indicate inclusion formation. Inclusions were observed forming a zone at the crystal periphery, figure 6.11a and at the central of the crystal figure 6.11b. Crystals produced with no rotation failed to show any inclusion formation in the crystal center. Inclusions at the crystal edge were only rarely observed and did not form a zone but rather were solitary in nature.
When Cd was added to the reservoir zone the pitting effects were further exacerbated, resulting in the formation of sponge-like material, figure 6.12a. The chips visible in this photograph are the result of sticking with the ampule and the resultant breakage upon removal. Qualitatively, the material was more highly reflective, metallic, than the material produced with no Cd added to the reservoir. Cross-sections which were cut out of the boule just prior to the onset of the spongy material showed metallic inclusions, figure 6.13a. SEM/EDX analysis, figure 6.13b, confirms that these inclusions are composed of Cd metal.

6.4.2 Discussion

The formation of sponge-like material can now be understood. It is a result of formation of Cd inclusions due to interface instability. The instability is probably due to growth from a melt of composition which is far from the congruent melt composition, resulting in a segregation coefficient far from 1. The enhanced segregation, which approaches the conditions of solution growth, leads to interface breakdown. When the volume fraction of inclusions is high enough to result in impingement, a 'channel' of Cd metal is formed. Since Cd metal has a significant vapor pressure extending to well below the CdTe solidification temperature, the metallic 'channels' have ample time to evaporate during postgrowth cooling. This phenomenon results in the formation of the cavernous 'channels' observed in the spongy material, figure 6.12b.

The same behavior can also account for the pits which form during high Pe growth in crystals with no Cd added to the reservoir. The differences may be understood when we consider that in the case of no Cd added to the reservoir, the amount of Cd rejected may be quite small. If we adjust
the reservoir temperature such that it is in equilibrium with a melt of Cd content greater than the one achievable by adding all the Cd in the reservoir to the remaining melt, the melt will not have that equilibrium composition. Instead, the Cd content will be lower and the interface will not breakdown as rapidly, as is observed.

The results also seem to indicate that rotation at constant velocity results in the formation of a boundary layer near the ampule wall and at the charge center. The observation of inclusions in crystals experiencing rotation but not in those grown without rotation supports this contention. Unfortunately, a more definitive statement is not possible at this time. Perhaps numerical analysis of the fluid flow in this system, with and without rotation applied, may yield insight into this area. Regardless, it seems clear that the application of rotation at constant velocity yields crystals of inferior quality. If these inclusions are indeed due to boundary layer formation, the application of accelerated crucible rotation may yield favorable results. It is expected that inverting the sense of the rotation will serve to break up any boundary layer formation, while still enhancing fluid flow.
Figure 6.9: Fluid flow analysis with and without rotation

No Rotation

Rotation
\( \sim 5 \text{ rpm} \)

\[ g = x \times 10^{-4} \]

maximum velocity

3.18 \times 10^{-4} \text{ cm/s} \quad 4.93 \times 10^{-4} \text{ cm/s}

Hot Zone
Figure 6.10: Correlation of external pits with reservoir temperature change
Figure 6.11: IR microscopy of the periphery and center of a boule grown with rotation
Figure 6.12: A: CdTe crystal growth with rotation and Cd added to reservoir. B: Expanded view of last to the freeze portion.
Figure 6.13: Metallic inclusions
6.5 The Influence of Seed Orientation

The utility of seeding in crystal growth is well known, it is a method of producing boules of a desired crystallographic orientation. However, it also has great utility in studies which attempt to understand the kinetics of various growth directions. In the present study, seeding experiments were conducted in order to discover if any preferred growth orientation exists for CdTe. The effect of crystallographic orientation on twin formation was also examined during this study. Full diameter and reduced diameter seeds oriented [100], [110], and [111] were utilized. The effectiveness of ampule constrictions, apertures, and regions of reduced diameter as a means of promoting grain selection was also examined.

6.5.1 Results

Initially experiments utilized crushed CdTe powder as a charge in an attempt to identify any preferred growth orientation. Powder was used since it provided a large number of exposed crystallographic orientations. A long tube of approximately 10 cm length was formed onto the end of a standard 16 x 20 mm quartz ampule. In an effort to facilitate grain selection, the melt-back interface was adjusted to allow growth, for a number of centimeters, in the reduced diameter tube. Figure 6.14a shows the region which propagated along the reduced diameter. The twins are nearly parallel to the growth axis indicating the growth direction is nearly perpendicular to a <111> direction. Laue taken on the sample shows the growth axis is actually very nearly <110>. The crystal propagates the entire length of the
reduced diameter without introducing additional twins and is single crystalline. When the reduced diameter tube begins to flair out so as to join the larger diameter ampule, the single crystal breaks down and polycrystalline material results, figure 6.14b.

Apertures were also used in an effort to encourage preferential grain selection. Figure 6.15a reveals the effect of a graphite aperture on the crystal growth. The design of this aperture was very simple lacking any tapers to accommodate diameter changes. The effectiveness of the aperture in selecting a grain is apparent. After the constriction, a singular grain comprises ~70% of the cross sectional area, figure 6.15c. The propagation of the selected grain through out the boule did not occur. The graphite aperture was not wet by the CdTe charge as is evidenced by the fact that the crystal could be removed after the aperture was cut in half. As can be seen in figure 6.15b, the twin lamellae are very nearly parallel to the growth axis. Laue indicates that the direction cosines of the grain propagating through the aperture are 0.8213, 0.5221, 0.2388, very close to a \{752\}. Confirming that a (111) plane is nearly perpendicular, i.e. 86.56°, to the growth axis. In the case of a BN aperture, wetting was apparently a problem since the crystal could not be removed even after the aperture was sliced in half.

Seeding was attempted in the three low index crystallographic orientation, namely [100], [110], and [111]. The experiments could be broken up into two groups, those using full diameter seeds and those using reduced diameter seeds. Obtaining full diameter seeds was problematic, therefore only the [110] and [100] directions were investigated using them\textsuperscript{32}. Although also difficult to obtain, reduced diameter seeds were used in the majority of the seeding experiments\textsuperscript{33}. Seeding in a [110] direction
resulted in the propagation of the seed orientation for large distances in the growing crystal. Figure 6.16a, shows the propagation of twin lamellae over long distances in the growing crystal. The crystal produced during this run produced a replication of the seed orientation for approximately 1.3 cm, figure 6.16b. Another grain forms and propagates at the expense of crystal in the seed orientation for \( \sim 6.8 \) cm. The crystal then reverts back to the seed orientation of [110] for the final 4.1 cm of growth. Figure 6.16c shows the first portion of the crystal to solidify in other than the seed orientation. Laue back reflection reveals the direction cosines of the new orientation are 0.797745, 0.184259, 0.580394, while those of the seed are 0.134644, 0.650965, 0.746510 in the cross-section. Analysis based on the techniques described in appendix G indicate that the two grains are in a fourth order twin relationship.

[111]B seeds of reduced diameter were also examined. The seeds were placed in a quartz tube of smaller diameter than the growth ampule. A neck was incorporated in the reduced diameter tube. For the most successful run, the [111]B orientation was propagated for approximately 2.5 cm through the reduced diameter seed holder and neck region. Upon exiting the neck region, the crystal changes orientation, finally ending up in a [110] type orientation, figure 6.17a. The [110] oriented crystal then propagates for 7.5 cm until a power failure terminates the run. Even after the power failure, the external portion of the crystal continues to propagate in the same orientation. The mechanism for changing crystallographic orientation was examined using Laue. Figure 6.17b is a cross-section of the neck region were the crystal changes orientation from the [111] seed orientation to the [110] orientation. As can be seen in the figure, the transition takes place via a third crystallographic orientation. The seed and the transition
grain do not appear to be related in any twinned relationship. However, the transition grain does appear to be in a twinned relationship with the propagating grain. Similar behavior was observed using [110] seeds, i.e. the seed orientation propagated up to the region of increasing diameter.

A limited number of experiment were conducted using [100] seeds. The resulting crystals did not show any indication of propagating the seed orientation. On the contrary [100] seeding appeared to initiate polycrystalline growth immediately. The results however do not preclude successful seeding using [100]. Due to difficulties obtaining seeds, the only seeds available consisted of more than one grain, with the major grain being [100]. If one were able to obtain completely single crystalline seeds in a [100] orientation, the seeds may propagate to produce single crystal. It does not however appear that [100] is a preferred orientation for growth, based on the data obtained in this study.

6.5.2 Discussion

The results of this study suggest that growth perpendicular to the <111> is preferred. Including but not limited to growth in the [110] direction. Evidence which supports this contention consists of the statistical prevalence of crystals which grow with their lamellar twins parallel to the growth axis. These crystals can be produced by heterogeneous nucleation, availability of large numbers of grains, selection by means of reduced area constrictions or apertures, and by intentional seeding. Twin lamellae which are perpendicular to the growth axis can be propagated for large distances.
The use of reduced diameter seeds is problematic, since the crystals tend to breakdown in the region where the crystal diameter is increasing. This behavior was observed for both [111], and [110] growth directions. The cause of this behavior is unknown, however, it is thought to involve enhanced heat transfer through the quartz seed holder. For CdTe the liquid has a larger thermal conductivity than the solid. Therefore, heat transfer between the charge and the ampule, leads to a concave interface, this is referred to as the interface effect. Jasinski et. al.\textsuperscript{87} have shown that the interface effect increases as the radius ratio between crucible and charge increases. Therefore, as the radius of the seed is reduced, the radius ratio between the crucible and charge effectively increase, which is expected to lead to a more concave interface. In an extreme case, the nucleation at the ampule walls may lead to 'pinching off' the propagating seed. The Laue patterns obtained from the portion of the seed orientation in the constriction had broad diffraction spots which are a qualitative indication of a high stress state. The propagating grain does not exhibit such behavior; its spots are well defined.
Figure 6.14: The effectiveness of a reduced diameter channel for grain selection
Figure 6.15: Grain selection resulting from the use of a graphite aperture
Figure 6.16: [110] Seeded growth of CdTe
Figure 6.17: [111] Seeded growth
6.6 Effects of Ampule Coating

A limited investigation of ampule coatings was conducted. The only coating which was used was pyrolytic graphite deposited on cleaned ampules by cracking of acetone. The effect of the coating on the resultant crystals was not dramatic. The only effect that could be correlated to graphite coating was a decrease in the tendency to stick to the ampule at room temperature. For graphite coated ampules sticking was never observed. While sticking to uncoated quartz ampules was not always a problem, it did occur in approximately 40% of the crystals grown. Sticking was consistently problematic for crystals which were grown far from the stoichiometric composition. This was observed on either the Cd rich or Te rich sides of the phase diagram, although based on only limited data for Te rich growth. Chemical analysis of the portion of a quartz ampule which had been adhered to, revealed traces of Ag, Al, Cu, and Mg in addition to Cd, Te, and Si. Although no definitive statement can be made relating the sticking at room temperature to the crystal quality, for cases of severe sticking, the crystal was invariably polycrystalline with small grains.

6.7 The Effect of Changes in Thermal Environment

By adjusting the temperatures of the heater and cooler and by changing the gradient zone length, the thermal environment in the vicinity of the growth interface was modified. Intuitively, it is expected that the interface should be concave when it is positioned near the cooler because heat should flow from the relatively hot charge to the cooler resulting in solidification near the edges.
Similar reasoning would lead to the conclusion that the interface would be convex when located near the heater. Therefore, we expect a favorable interface shape when the interface is located near the top of the gradient zone. Increasing the axial gradient is expected to increase the magnitude of the axial heat flow and thereby decrease the interface curvature, suggesting more favorable growth conditions can be obtained by using higher axial gradients.

6.7.1 Results

To gain semi-quantitative insight into the magnitude of these changes, the analytical heat transfer model developed by Jasinski\textsuperscript{134} was used to predict the axial interface position, and the interface curvature. Justification for the approach can be made by considering the excellent agreement between the interface position predicted by the model and that observed, table 3. Jasinski's model calculates a radial temperature gradient between fins. Three fins are considered an inter charge fin, an outer charge fin and the crucible. In the present analysis, the radial gradient between the two charge fins is ratioed to the axial gradient calculated using the model. The magnitude of this quantity is taken to be indicative of the magnitude of the interface curvature.

To move the melt-solid interface closer to the cooler, the temperature of the heater and cooler are increased. In an effort to maintain a constant interfacial gradient the difference between heater and cooler temperature is kept constant. The maximum distance the interface can be moved is then limited by the maximum operating temperature of the hot and cooler zones. By operating the heater zone at 1180°C and the cooler at 1050°C the interface was moved approximately 4 cm, closer to the cooler. In this case the
maximum operating temperature of the heat pipe limits further movement. Figure 6.18 contains the results of a unseeded growth experiment using these conditions. Only a few grains are visible in the regrown portion of the boule. Twin lamellae extend the entire length of the boule, indicating the existence of a singular orientation. The observed behavior is not significantly different than results obtained when the interface was placed close to the heater, figure 6.16. Using the heat transfer model, the gradient ratio for the system with the interface near the cooler is $8.9 \times 10^{-3}$ while for the interface near the cooler it is $8.6 \times 10^{-3}$. This counter intuitive result indicates that there should be slightly less curvature near the bottom of the gradient zone.

In order to obtain steeper axial gradients, the temperature difference between the heater and the cooler may be increased, or the gradient zone length may be reduced. There are constraints to both approaches. The maximum temperature of the heater is limited in the present configuration by the use of a Ni heat leveler. If the gradient is increased by lowering the temperature of the cooler without increasing the temperature of the heater, the interface moves nearer to the heater into a region of nonlinear and decreasing axial gradient. It is therefore conceivable that increasing the temperature difference could result in a decrease in the axial gradient. Reducing the gradient zone length results in an increase in the roundoff observed in both zones. The effect is more severe in the Ni heat leveler than in the heat pipe as discussed in section 4.5. The net result is an effective gradient zone length which is larger than would be expected based on the actual reduction in length of the gradient zone. The experimental program consisted of using a smaller gradient zone 3.56 cm and zone temperatures of 1150°C for the heater and 900°C for the cooler. Figure 6.4 shows the results of an high gradient
unseeded growth run which spontaneously grew single crystalline until a high growth rate was imposed on the system. Laue back reflection identified the growth axis to be nearly [211]. Other runs using similar conditions led to the growth of large grain polycrystalline CdTe. The dislocation density as revealed by etching did not seem to increase due to increased axial gradients. Using the heat transfer model the gradient ratio is calculated as $7.7 \times 10^{-3}$ which indicates that less curvature is expected in the case of higher axial gradients.

6.7.2 Discussion

The calculated gradient ratios can be used to estimate the degree of curvature of the interface using the following approximation.

$$\frac{r}{R} \approx \frac{\Delta T_r}{\Delta T_a}$$

Where:  
$r \equiv$ Maximum deflection of the interface  
$R \equiv$ Radius of the charge  
$\Delta T_r \equiv$ The radial temperature gradient  
$\Delta T_a \equiv$ The axial temperature gradient

Calculations indicate the largest maximum deflection of the interface (MDI) is $\sim 71 \, \mu m$ for the interface near the top of the gradient zone in the low gradient configuration. The smallest MDI is expected to be $\sim 62 \, \mu m$ for the high gradient configuration, corresponding to approximately a 15% change in interface curvature. For the interface moved to near the bottom of the gradient zone while using a low gradient, the MDI is $\sim 69 \, \mu m$ or only a $\sim 3\%$ change. The magnitude of the expected interface curvature is well below the resolution of the measured interface shape, section 4.5, and is therefore consistent. Concave interfaces were predicted by the model
in all instances. The unexpected decrease in the predicted interface curvature when moved nearer to the cooler was due to an increase in the axial gradient. The radial temperature gradient did increase as expected. In general the experimental results did not reveal any strong dependence of the crystalline quality with either the interface position in the gradient zone or the axial gradient. However, based on the data one may argue that a large axial gradient is more favorable to the propagation of single crystals. Unfortunately it is difficult to quantify the observed growth behavior. The predicted interface curvatures using the model help explain the observed behavior by suggesting that the effect of the containment dominates the heat transfer.
Figure 6.18: Crystal grown with interface near cooler
Chapter 7

Analysis and Conclusions
7.1 A Discussion of Twinning in CdTe

The origins of twinning in CdTe are still unclear, however some commentary can be made in light of recent experimental results. Twin free material could not be produced in the present study but material which did not add new twins to twins already present in the seed could. It therefore may be that given a twin free seed in the appropriate orientation, e.g. [110], a twin free crystal may be produced. Twins which are perpendicular to the growth axis have been observed to propagated over large distances. The nucleation mechanism for twin formation has not been isolated, however based on the limited data obtained in this study that [100] growth is not favored, it does not appear that it is simply a kinetically driven mechanism. Assuming the mechanisms proposed by Szilagyi" are operating, the data suggest a clustering and attachment mechanism may dominate. The observed peak in the liquidus at the congruent melting point, figure 2.1, serves as evidence of clustering in the melt, as does the electrical behavior in the vicinity of the melting point."

7.1.1 A theoretical basis for twinning in ionic semiconductors

Although the nucleation mechanism for twin formation remains unresolved, the ease of twinning can be understood on a theoretical basis. The analysis begins by recognizing that viewed locally, a twin in the zincblende structure is the smallest recognizable volume of a wurtzite phase. It may therefore be argued that the energetics may be similar. Based on theoretical considerations the wurtzite structure is
expected to be stabilized by greater ionic bond nature. This can be understood by recognizing that the nearest neighbor and next nearest neighbor bond distances are identical for both structures. The third nearest neighbor distances for wurtzite are smaller than for zincblende, since these sites are occupied by unlike atoms the effect of ionicity is attractive, thus stabilizing. Examination of the Madelung constants for these structures also confirms this analysis. Following Sherman\textsuperscript{135} the ionic contribution to the lattice energy may be expressed as the following.

\[ \tilde{\varepsilon}_0 = -\left( \alpha^2 \mu e^2 A \right) / R_0 \]

where

- \( e \) = Unit of electrostatic charge \( 4.770 \text{ E.S.U.} \)
- \( \alpha \) = The largest common factor in the valences of all the ions
- \( \mu \) = The number of stoichiometric molecules in the unit cell
- \( A \) = The Madelung constant which is dependent only on crystal structure
- \( R_0 \) = Equilibrium bond length obtained using x-ray data.

When comparing the energies of zincblende and wurtzite, the equation simplifies to a negative constant multiplied by the Madelung constant. The Madelung constant for zincblende has been calculated\textsuperscript{136, 137, 138} to be 1.63806 while that for wurtzite is 1.641. Although the wurtzite structure is more stable using this analysis, it is important to realize the energies between these structures is quite small.

Comparing the degree of ionicity and the crystal structures for the II-VI compounds aids in understanding the chemistry involved for CdTe. Table 5 is a compilation of the Pauling electronegativities for the IIB and VIB elements. While in table 6 the structures for the II-VI compounds are examined. The first crystal structure listed in the table is
Table 5: Pauling electronegativities for the IIB and VIB elements

<table>
<thead>
<tr>
<th>IIB</th>
<th>Electronegativity</th>
<th>VIB</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.65</td>
<td>O</td>
<td>3.44</td>
</tr>
<tr>
<td>Cd</td>
<td>1.69</td>
<td>S</td>
<td>2.58</td>
</tr>
<tr>
<td>Hg</td>
<td>2.00</td>
<td>Se</td>
<td>2.55</td>
</tr>
<tr>
<td>*</td>
<td>*</td>
<td>Te</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 6: Structures of II-VI compounds

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>W</td>
<td>Z,W</td>
<td>Z,W</td>
<td>Z</td>
</tr>
<tr>
<td>Cd</td>
<td>NaCl</td>
<td>W,Z</td>
<td>W,Z</td>
<td>Z</td>
</tr>
<tr>
<td>Hg</td>
<td>Or,Rh</td>
<td>Z,Tr</td>
<td>Z</td>
<td>Z</td>
</tr>
</tbody>
</table>

Z = Zincblende, W = Wurtzite, Or = Orthorhombic, Rh = Rhombohedral, Tr = Trigonal: The first structure listed is the most prevalent at Tr, P63.

The most commonly observed phase at room temperature and atmospheric pressure.

Examination of Pauling electronegativities indicates that compounds composed of a given cation become less ionic as the anion atomic number increases. The electronegativities also point out that Hg has a greater affinity for its electrons than does either Zn or Cd. We see for the compounds based on Zn the structure is wurtzite for the more ionic compounds and tends to zincblende as the ionicity decreases. For those compounds of intermediate
ionicity, we see both structures are stable and the compounds exhibit stacking faults. Similar behavior is observed in those compounds based on the Cd cation. We see however that in this series the ionicity is somewhat larger than in the Zn series. This is evidenced by the NaCl structure for CdO which has a coordination number of 6 and is indicative of ionic bonding, moreover the wurtzite structure is the most prevalent for the sulfide and selenide. The Hg based compounds are never observed in the NaCl or wurtzite structures as would be expected considering the decreased ionicity expected based on the electronegativity of Hg. In view of the approximate nature of the electronegativity any conclusions based on this data are necessarily qualitative. However, these qualitative conclusions aid in understanding the chemistry of these compounds.

Based on the trends observed, we may conclude that CdTe is near to the ionicity value which results in both wurtzite and zincblende being stable at standard conditions. Therefore it follows that the energy separating the zincblende structure from that of wurtzite in CdTe is probably small. Although in bulk crystals, zincblende is the equilibrium structure, polytypes have been observed in CdTe thin crystals\textsuperscript{39}. As expected, the most prevalent polytype is wurtzite which is observed as a metastable phase in thin films. The growth conditions which favor the formation of the wurtzite phase in thin films are still debated\textsuperscript{1}. With explanations based on temperature of the substrate and/or source, and stoichiometric deviations yielding conflicting results.

Figure 7.1 contains high resolution electron microscopic (HREM) evidence revealing a phase transformation during electron beam heating. The fringes observed are due to the (111) planes in CdTe. The featureless region near the perforation was observed to expand at the expense of the

- 170 -
matrix. Eventually, fringes appear which do not correspond to higher order interference effects due to the {111}. Measuring the spacing of these new fringes indicates that they are consistent with a wurtzite transformation. The driving force for the transformation may be surface effects since the region where it is observed is very thin. Furthermore, mobility of CdTe under electron beam heating has been reported in the literature\textsuperscript{140-142}. The evidence therefore suggests the energy separating the wurtzite and zincblende structures is small for CdTe, due to its relatively high ionicity. It is expected that the energy between the twinned and untwinned structures will also be small, again due to the ionicity of CdTe. Gottschalk et. al.\textsuperscript{143} have found excellent agreement between the reduced stacking fault energy, which can be related to the twin plane energy, and the Philips ionicity for III-V compound semiconductors, with the stacking fault energy decreasing linearly with increasing ionicity. Unfortunately, the stacking fault energies for only a few of the II-VI compounds are known therefore, a similar study has been impossible.
Figure 7.1: In situ phase transformation under electron beam irradiation
7.1.2 Twinning and its effect on electrical properties

It would be expected that since twins do not involve any broken bonds, their effect on the electrical properties would be minimal. In this section a mechanism for the attraction of dislocations to twins will be developed. This mechanism will offer explanation as to the detrimental aspects of twinning on the electrical properties of CdTe. Furthermore, the accumulation of dislocations to twins provides heterogeneous nucleation sights for the formation of precipitates. The effect could also lead to the formation of low angle grain boundaries. The derivation is based on transforming the Burgers vector on a slip system based on a theoretical twin transformation matrix and calculating the force between two parallel dislocations to determine the interaction between them.

In this analysis the results of Hall\textsuperscript{110} are used as a justification to consider only edge type dislocations. His high temperature deformation experiments showed that under low strain (\textless 12\%) conditions the predominant dislocations observed were edge type on a single slip system with Burgers vector a/2[1-10]. The maximum strain experienced during growth would occur if we had complete wetting of the ampule and cooled down allowing differential expansion to deform the material. The thermal expansion coefficient for CdTe above 300\textdegree K is flat at approximately 6\times10^{-6}/\textdegree C\textsuperscript{1}. Assuming the conservative case of a 1100\textdegree C temperature change the corresponding strain is about 6.6\times10^{-3} or 0.7\% strain. This is well below the 12\% strain and justifies the simplifying assumptions of considering only edge type dislocations on a single slip system. The approach for screw dislocations is similar but will not be derived here.
The transformation of a Burgers vector across a twin is obtained by matrix multiplication of the Miller indices by the twin transformation matrix.

\[ b' = T \cdot b \]

Where:

- \( b' \) = Miller indices of the Burgers vector after a twin transformation
- \( T \) = The twin transformation matrix
- \( b \) = The original Burgers vector

The determination of the twin transformation matrix is based on the known axis-angle transformation pair. A detailed description including references is included in the appendices. For the zincblende crystal structure, the axis-angle transformation is a 180° rotation around \( \langle 111 \rangle \). For illustrative purposes, the results of a rotation about the [111] will be used in our discussion, the effect is however general.

\[
\begin{pmatrix}
-1 & 2 & 2 \\
1/3 & 2 & -1 \\
2 & 2 & -1 \\
\end{pmatrix}
\]

Twin transformation matrix

180° rotation around [111]

The transformation of the \( a/2[-101] \) Burgers vector observed by Hall is then \( a/2[10-1] \). This is equivalent to an inversion of the Burgers vector, and occurs for all Burgers vectors which lie in the plane whose normal is the twin rotation axis.

The force between two parallel straight dislocations can be shown\(^{12}\) to follow the form:
A Radial term:
\[ F_r / L = \mu / (2\pi R) (b_1 \cdot X) (b_2 \cdot X) + \mu / (2\pi (1-v) R) [(b_1 \times X) \cdot (b_2 \times X)] \]

A \( \theta \) term:
\[ F_\theta / L = \mu / (2\pi (1-v) R^2) [(b_1 \cdot \hat{r}) [(b_2 \times \hat{r}) \cdot X] + (b_2 \cdot \hat{r}) [(b_1 \times \hat{r}) \cdot X]] \]

The total force per unit length is the linear combination of these terms.
\[ F_t / L = F_r / L + F_\theta / L \]

Where:

- \( L \) = length of dislocation
- \( b \) = Burgers vector (subscript indicates dislocation)
- \( X \) = Line direction of dislocation (both taken to be the same)
- \( R \) = Separation of dislocations
- \( \hat{r} \) = Unit vector in the radial direction separating the dislocations
- \( \mu \) = Shear modulus
- \( v \) = Poisson's ratio
- \( F \) = force on dislocation

Using the fact that at high temperature and low strain the dislocations are edge type we can simplify since for edge dislocations \( b \cdot X = 0 \), and the twin transformation is equivalent to inverting the Burgers vector of the dislocation so \( b_1 = -b_2 = b \).

The Radial term:
\[ F_r / L = \mu / (2\pi (1-v) R) [(b \times X) \cdot (-b \times X)] \]
\[ F_r / L = -\mu b^2 / (2\pi (1-v) R) \]

The \( \theta \) term:
\[
F_e / L = \mu / (2\pi (1-\nu) R^3) \{(b \cdot \hat{r})(-b \cdot \hat{r}) + (b \cdot \hat{r})(b)\}
\]

\[
F_s / L = \mu / (2\pi (1-\nu) R^3) \{(b \cdot \hat{r})(-b) + (-b \cdot \hat{r})(b)\}
\]

\[
F_F / L = -\mu b^2 / (2\pi (1-\nu) R^3) \{2\cos(\theta)\}
\]

Where \( \theta \) = The angle between the positive sense of the Burgers vector the radial vector separating the dislocations.

The total force on the dislocations is:

\[
F_t / L = -\mu b^2 / (2\pi (1-\nu) R) \{(R^2 + 2\cos(\theta))/R^2\}
\]

The importance of this result is that the force is always negative and the dislocations will therefore attract each other. A similar result could be derived for screw dislocations. Thus twin boundaries with rotation axis equal to the normal to the slip plane of dislocations will tend to 'sink' the dislocations. This will form a hybrid structure which has broken bonds and excess volume to serve as a heterogeneous nucleation site for precipitation.

There is also experimental evidence that suggests that twins do attract dislocations. In figure 7.2a an IR micrograph shows a CdTe crystal which has a linear array of decorated dislocations and can be seen terminating at the surface of the crystal in a straight line. Thru focus microscopy confirms that the dislocations lie on flat planar defects. This suggests that they are indeed lying in the composition plane of the twin. The region which does not show any dislocations can be understood if we consider a twin plane whose rotation axis is not the normal of the slip plane. For this type of dislocation the Burgers vector is not inverted by the twin transformation. The force between dislocations on opposite sides of the twin are therefore not necessarily attractive. At low stress, we anticipate that predominantly one slip system is activated during high
temperature deformation. This suggests that if the twin plane rotation axis and the slip plane normal do not coincide, there would be a considerable probability that the twin would not sink dislocations. Figure 7.2b shows an etched surface which has a boundary where etch pits of the opposite sense are coincident with each other. This is exactly the behavior which is predicted by the above theoretical analysis. The attractive behavior of dislocations of the opposite sense at twin boundaries has been previously observed in the literature\textsuperscript{44}, however it was not reported as such or described. The behavior of twins therefore can easily account for their observed detrimental effect on electrical properties.
Figure 7.2: A: IR micrograph of CdTe showing the alignment of dislocations to twin boundaries. B: Coincidence of etch pits of the opposite sense on a twin boundary.
7.2 Origins of Polycrystallinity in CdTe

The difficulty in producing single crystalline boules of CdTe is well established in the literature. During the present research program three apparently independent mechanisms leading to polycrystalline breakdown have been identified. They are as follows:

1. Interface breakdown due to constitutional supercooling, i.e. an unfavorable growth rate or gradient

2. Nucleation of crystals at the ampule wall due to unfavorable heat transfer, i.e. interface shape, or severe wetting of the ampule

3. High order twinning phenomena

Since polycrystalline material results if any of the above mentioned mechanisms are activated, it is understandable that single crystalline growth of CdTe has been so elusive. The data suggest optimization of the growth rate for a given set of furnace conditions can be accomplished relatively easily. Problems with heat transfer also do not seem to be the dominant source of polycrystalline breakdown. Heat transfer related problems did seem to dominate in regions of reduced diameter where the crucible thickness became significant in relation to the charge diameter. It is expected that interface curvature related problems can be relatively easily reduced to secondary levels. The problem of wetting of the ampule is very difficult to evaluate, and even more difficult to control. If wetting is indeed the dominant mechanism for polycrystalline growth, one would expect that the initiation of the secondary grains should occur at the ampule walls. In the present study such growth behavior was observed while all
available data relating to the interface shape suggest that it was planer. Furthermore, the relatively high dislocation densities observed as high as \( \sim 10^6/\text{cm}^2 \) suggest that wetting and differential contraction is a dominant mechanism. In addition to mechanisms 1 and 2, which are present in varying degrees for all materials, CdTe which has a low twin plane energy has another mechanism which can result in polycrystalline breakdown. Grains which were related in a high order twin relationship were observed in the course of this research. In general, boules in which this behavior was observed consisted of a few large grains. Since the tendency to twin is a materials property, the only mechanism available to influence high order twin formation is by altering the chemistry of the material, i.e. alloying or doping. In the previous section 7.1.1 the ionicity of CdTe was identified as a cause of its low twin plane energy. Using simple electronegativity a guide, alloying with Hg would be expected to reduce the tendency for twinning which is the behavior observed in the literature. Based on the crystal structures observed for the Zn chalcogenides, alloying with this element would also be expected to reduce the tendency for twinning. The effectiveness of doping to reduce the tendency of CdTe to twin has not been studied to my knowledge.

7.3 The Nature of Precipitates in CdTe

The evidence obtained during the course of this study has shown the existence of a retrograde solidus on the Te rich side of the phase diagram is a source of precipitation in CdTe, with Te precipitates being identified using STEM analysis. Furthermore, the data suggest control of the vapor pressure of cadmium can be an effect method of eliminating these precipitates. A reservoir temperature of 750°C has resulted in crystals which exhibit few precipitates. The
sensitivity of the microstructure to vapor pressure has not been extensively characterized, however, it appears to be a slowly varying function of reservoir temperature for temperatures below 750°C. The density of the precipitates observed with reservoir temperatures above 750°C is negligible. Reservoir temperatures above 800°C resulted in the formation of Cd inclusion, polycrystalline material, and finally spongy material, so the Cd rich side of the phase diagram could not be examined extensively. Precipitates were observed in greater numbers in regions of the crystal which contained a large number of dislocations. Indeed it appears as though they are acting to pin dislocation motion, figure 7.3, which could explain the increase in critical resolved shear stress which has been reported in the literature with deviation from stoichiometry. Other precipitates were observed which were composed of impurities, these were found to contain Fe, Al, Mg, Cu, and Si. The source of these impurities is not well known at this time.
Figure 7.3: Precipitates decorating dislocations in CdTe, using different sample tilts.
7.4 Optimized Growth Conditions for CdTe

Although no process for the growth of single crystalline boules has been developed, a number of trends have been identified which result in crystal of better quality. These are listed below:

- Low growth rates, 0.2 cm/hr resulted in the best crystals, however lower growth rates were not explored, and may yield improved results.

- Reservoir zone set point of 750°C which reduced the density of precipitates. Temperatures above this value virtually eliminated spherical Te precipitates, however growth was complicated by an increased tendency to form inclusions of Cd.

- The use of full diameter seeds yielded better quality crystals. Regions of increasing crystal, ampule, diameter invariably initiated polycrystalline growth.

- Seeding in a [110] orientation which resulted in propagation of the seed orientation. This is a subset of all directions which are perpendicular to <111>. Very promising results were serendipitously obtained for <211> growth.

- High axial gradients appear to enhance grain selection. The maximum gradient examined was nominally 40°C/cm. The diameter of the ampules should be increased so as to maximize the effectiveness of heat transfer control available in the furnace. Calculations indicate that the influence of the furnace is greatly reduced due to the ampule.
This page intentionally left blank.
- Graphite coated ampules, eliminated the sticking observed at room temperature.
Chapter 8

Summary and Suggestions for Future Work
8.1 Summary

The following summarizes the major findings of this study:

- A furnace system with well defined thermal boundary conditions and the ability to control the vapor pressure over the melt has been designed and constructed. The system behavior agrees well with predictions based on a previously developed analytical model of heat transfer in a system with similar boundary conditions. The interface appears to be planar to within the measurement resolution of \( \sim 0.05 \) cm. Quasi steady state growth has been demonstrated using interface demarcation in Ga doped Ge\(^{103}\).

- Growth rates greater than 0.2 cm/hr were found to produce material with a high density of precipitates. As the growth rate increases from 0.6 cm/hr to 1.2 cm/hr the average size of the precipitates increases and inclusion begin to appear. Increasing the growth rate further, to 2 cm/hr initiated polycrystalline growth. The cause of the polycrystalline breakdown is apparently due to constitutional supercooling.

- Reduced diameter necks, apertures, and constrictions were found to be effective for grain selection. However, when the reduced diameter regions of the ampule were increased to join with the main ampule, polycrystalline growth almost invariably occurred. The best results were obtained when the reduced diameter was nearly the same as the ampule diameter, and tapers were avoided.
- Reproducible seeding was successfully achieved in a vertical Bridgman/Stockbarger configuration. The reproducibility of the interface position for a given set of furnace conditions was approximately ±0.1 cm. The interface position could be predicted to within ±0.2 cm using an analytical heat transfer model.

- <110> growth was identified as a preferred growth axis. This observation may actually be a special case of a more general preferred orientation i.e. directions perpendicular to <111>. High quality crystals were observed to propagate along <211>, and <752> axes. Some limited success was observed for <111> growth. [100] seeding initiated polycrystalline growth.

- Graphitization of ampules eliminated sticking at room temperature. The dislocation density observed, which ranged from below $10^4$ /cm$^2$ to above $10^6$ /cm$^2$, was not significantly altered which suggests that wetting at temperature may still be a problem.

- Precipitate density was found to be a function of reservoir temperature, suggesting effective mixing in the liquid phase exists. For reservoir temperatures below 750°C spherical precipitates of nominally 5 μm diameter are observed. The density of the precipitates increases as the reservoir temperature is decreased. STEM analysis indicates that the precipitates are composed of Te. For crystals grown with reservoir temperatures above 750°C virtually no spherical precipitates were observed. Growth with reservoir temperatures above 800°C resulted in an enhanced tendency to form inclusions. The inclusions were identified to be composed of Cd by SEM-EDX. An enhanced density of precipitates was observed in regions of the crystal which had large densities of
dislocations. The precipitates appeared to decorate the dislocations, which may explain the observed increase in resolved shear stress observed for off stoichiometric material*. *.

- Rotation of the ampules at a constant velocity of ~17 rpm was found to lead to the formation of inclusions at the crystal periphery and center. This is believed to be due to the formation of boundary layers.

- The prevalence of twinning in CdTe is explained as being due to its significant ionicity. Twins are shown to act as sinks of dislocation in certain circumstances. It is concluded that the attachment of twin nuclei to the propagating interface is probably the dominant nucleation mechanism for twin formation in CdTe.

- Three modes of polycrystalline breakdown have been identified. These are constitutional supercooling, nucleation at the ampule wall, and high order twinning phenomena.

8.2 Suggestions for Future work

Some areas which require more extensive evaluation are summarized below.

- The inability to produce undoped n-type CdTe from the melt is in need of more extensive evaluation. The observed formation of Cd inclusions with reservoir temperatures on the Cd rich side of the phase field suggest that the growth rates/thermal gradient used may have been too high. From the solidus we anticipate that a liquid composed of 54% Cd should yield
stoichiometric material this composition corresponds to a reservoir temperature of ~950°C which was not achievable in the present configuration at growth rates of 0.2 cm/hr and thermal gradients ~20°C/cm.

- Forced convection by accelerated crucible rotation may help reduce the tendency of inclusion formation and polycrystalline breakdown to allow more rapid growth rates to be utilized. The inversion of the sense of the rotation is expected to breakup any boundary layers which may form.

- A continuation of the investigation of the effect of seeding. New orientations such as [211] should be investigated. This orientation has been observed to yield single crystals for ribbon growth of Si, it has also produced high quality crystals in the present study. A repeat of <111> seeded growth should be conducted using full diameter seeds.

- Alloying with Zn or Hg may reduce the tendency for twin formation in CdTe and should be investigated. Recently published\cite{145, 146} results tend to indicate that larger fractions of boules can be produced single crystalline for CdZnTe than for CdTe. Dopants may also help reduce the tendency toward twinning, however the mechanism is not clear.

- The diameter of the charge should be increased. Calculations indicate that the effectiveness of the heat transfer control attainable in the present configuration is largely masked by the ampule. Short of revolutionary new ampule materials or composites, the most readily available method of reducing the influence of the ampule is to increase its diameter. Recent results\cite{147, 146} have indicated superior single
crystalline fractions are attainable in large diameter systems.

- Interface demarcation by current pulsing may provide higher resolution data for the interface shape, as well as growth rate data. This would require electrical feedthru to be constructed since the vapor pressure of CdTe is significant. By growing on the Te rich side the vapor pressures can be reduced.
Appendix A

Partial Vapor Pressure Calculations

The following section outlines the theoretical approach used to calculate the partial vapor pressure as a function of composition.

Using the Regular Associated Solution model developed by Jordan, the liquidus curve can be expressed as follows.

\[ T_{liq} = \frac{\alpha (X_t - 0.5) + \Delta H_r}{R/2 \ln(S(X_t)) + \Delta S_r} \]

Where:

\[ S(X_t) = \frac{((1+P)/(1+B))^2}{4 X_c X_t} \]

\[ P = (1 - 4 X_c X_t (1-B))^{1/2} \]

\[ X_t \equiv \text{The atomic fraction of component i}; \]

\[ \alpha \equiv \text{A constant, kcal}; \]

\[ B \equiv \text{A constant, dimensionless}; \]

\[ \Delta H_r \equiv \text{Heat of fusion, kcal/g-atom}; \]

\[ \Delta S_r \equiv \text{Entropy of fusion, kcal/g-atom K}; \]

Based on the work of Kulwicki, the heat of fusion at the congruent melting point has been reported as:

\[ \Delta H_r = 12.0 \pm 1.9 \text{ kcal/mole} \]

combined with the congruent melting point temperature of 1092°C allows the calculation of the entropy of fusion:
\[ \Delta S_r = 44.94 \text{ cal/mole K} \]

Jordan fits his model to the experimental results of Kulwicki, Lorentz, and deNobel and determines values for \( \alpha \) and \( \beta \) these are summarized below.

For the Cd rich subsystem:

\[ \alpha = 10.9 \text{ kcal} \quad \beta = 0.055 \]

For the Te rich subsystem:

\[ \alpha = 3.1 \text{ kcal} \quad \beta = 0.055 \]

Using the familiar thermodynamic relationship listed below allows us to calculate the component vapor pressure given the activity,

\[ p_i = p_{i0} a_i \]

Where:

\( p_i \) \equiv The partial pressure of \( i \);

\( p_{i0} \) \equiv The pressure over pure \( i \);

\( a_i \) \equiv The activity of component \( i \);

Again following Jordan, the activity can be expressed with the following equations,

\[ a_{C_{Cd}} = \frac{(X_{C_{Cd}} - X_{Te} + P) \exp(\alpha X_{Te}^i / RT)}{1 + P} \]

\[ a_{Te} = \frac{(X_{Te} - X_{C_{Cd}} + P) \exp(\alpha X_{C_{Cd}}^i / RT)}{1 + P} \]

Baker\textsuperscript{149,150} has established the vapor pressures of Cd and Te over their pure elements. The following equations represent the best fit to his data.
\log(P_{L'}) = -5730/T -1.15 \log T + 8.9850

\log(P_{f'}) = -6447.0/T -1.0 \log T + 8.1945

The calculation procedure is as follows:

1. Calculate the liquidus temperature for a given composition

2. Using the calculated liquidus temperature and the composition determine the activity coefficient

3. Using the liquidus temperature calculate the vapor pressure over the pure component

4. Determine the partial vapor pressure over the melt at the liquidus temperature

Table 7 summarizes the results of these calculations.
<table>
<thead>
<tr>
<th>$X_Te$</th>
<th>$\log(P_{Te})$ Atm</th>
<th>$\log(P_{Cd})$ Atm</th>
<th>$T_{calc}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010000</td>
<td>-0.343816</td>
<td>-3.530088</td>
<td>700.122978</td>
</tr>
<tr>
<td>0.020000</td>
<td>0.014688</td>
<td>-3.010326</td>
<td>770.527352</td>
</tr>
<tr>
<td>0.030000</td>
<td>0.205062</td>
<td>-2.729932</td>
<td>812.813000</td>
</tr>
<tr>
<td>0.040000</td>
<td>0.328092</td>
<td>-2.545928</td>
<td>842.369180</td>
</tr>
<tr>
<td>0.050000</td>
<td>0.415027</td>
<td>-2.413892</td>
<td>864.493956</td>
</tr>
<tr>
<td>0.100000</td>
<td>0.624577</td>
<td>-2.082222</td>
<td>923.322788</td>
</tr>
<tr>
<td>0.150000</td>
<td>0.697579</td>
<td>-1.955360</td>
<td>946.689460</td>
</tr>
<tr>
<td>0.200000</td>
<td>0.730745</td>
<td>-1.890453</td>
<td>958.508418</td>
</tr>
<tr>
<td>0.250000</td>
<td>0.754090</td>
<td>-1.836532</td>
<td>967.990015</td>
</tr>
<tr>
<td>0.300000</td>
<td>0.778803</td>
<td>-1.763412</td>
<td>980.216968</td>
</tr>
<tr>
<td>0.350000</td>
<td>0.804384</td>
<td>-1.645430</td>
<td>998.623272</td>
</tr>
<tr>
<td>0.400000</td>
<td>0.813874</td>
<td>-1.451320</td>
<td>1025.721001</td>
</tr>
<tr>
<td>0.450000</td>
<td>0.744229</td>
<td>-1.120437</td>
<td>1062.319007</td>
</tr>
<tr>
<td>0.460000</td>
<td>0.705002</td>
<td>-1.026085</td>
<td>1070.320295</td>
</tr>
<tr>
<td>0.470000</td>
<td>0.649393</td>
<td>-0.917699</td>
<td>1078.075922</td>
</tr>
<tr>
<td>0.480000</td>
<td>0.571621</td>
<td>-0.793352</td>
<td>1084.998904</td>
</tr>
<tr>
<td>0.490000</td>
<td>0.466419</td>
<td>-0.654300</td>
<td>1090.077366</td>
</tr>
<tr>
<td>0.500000</td>
<td>0.022989</td>
<td>-0.822515</td>
<td>1092.001365</td>
</tr>
<tr>
<td>0.510000</td>
<td>-0.133699</td>
<td>-0.680722</td>
<td>1089.900198</td>
</tr>
<tr>
<td>0.520000</td>
<td>-0.286085</td>
<td>-0.568317</td>
<td>1084.293258</td>
</tr>
<tr>
<td>0.530000</td>
<td>-0.424728</td>
<td>-0.485840</td>
<td>1076.497743</td>
</tr>
<tr>
<td>0.540000</td>
<td>-0.548610</td>
<td>-0.427386</td>
<td>1067.534287</td>
</tr>
<tr>
<td>0.550000</td>
<td>-0.659795</td>
<td>-0.386817</td>
<td>1057.998841</td>
</tr>
<tr>
<td>0.600000</td>
<td>-1.096492</td>
<td>-0.329227</td>
<td>1009.138870</td>
</tr>
<tr>
<td>0.650000</td>
<td>-1.432644</td>
<td>-0.380844</td>
<td>962.888933</td>
</tr>
<tr>
<td>0.700000</td>
<td>-1.726611</td>
<td>-0.479569</td>
<td>919.464374</td>
</tr>
<tr>
<td>0.750000</td>
<td>-2.006388</td>
<td>-0.609263</td>
<td>877.440697</td>
</tr>
<tr>
<td>0.800000</td>
<td>-2.295072</td>
<td>-0.770566</td>
<td>834.669583</td>
</tr>
<tr>
<td>0.850000</td>
<td>-2.623499</td>
<td>-0.978455</td>
<td>787.810992</td>
</tr>
<tr>
<td>0.900000</td>
<td>-3.052507</td>
<td>-1.275752</td>
<td>730.526966</td>
</tr>
<tr>
<td>0.950000</td>
<td>-3.769548</td>
<td>-1.808683</td>
<td>645.581202</td>
</tr>
<tr>
<td>0.960000</td>
<td>-4.002640</td>
<td>-1.987436</td>
<td>620.746617</td>
</tr>
<tr>
<td>0.970000</td>
<td>-4.305925</td>
<td>-2.222483</td>
<td>590.296373</td>
</tr>
<tr>
<td>0.980000</td>
<td>-4.738703</td>
<td>-2.561325</td>
<td>550.193131</td>
</tr>
<tr>
<td>0.990000</td>
<td>-5.491057</td>
<td>-3.156293</td>
<td>488.631018</td>
</tr>
</tbody>
</table>

Table 7: Calculated Vapor Pressures for Cd and Te as a Function of Composition

===============================================================================

- 195 -
Appendix B

Calculation of PID Constants

The following section outlines the method used to calculate the PID constants for the furnace system. The system was adequately modeled using a first order system response. Figure B.1 contains a block diagram of the system model used in the following derivation. The transfer function for the system can be shown to be of the form:

\[
\frac{C(s)}{R(s)} = \frac{G_1 G_2}{1 - G_1 G_2 H_1}
\]

Where:
- \( G_1 \) \equiv The transfer function for the PID
- \( G_2 \) \equiv First order system transfer function
- \( H_1 \) \equiv The feedback transfer function

The transfer functions mentioned above are well known.

For the PID controller:

\[ G_1 = \frac{K_p (1 + T_1 s + T_1 T_d s^2)}{T_1 s} \]

For the 1st order system:

\[ G_2 = \frac{R}{\tau s + 1} \]

For the feedback, unit gain:

\[ H_1 = -1 \]

Where:
- \( K_p \) \equiv Proportional constant
- \( K_d \) \equiv Derivative constant
\[ K_i \equiv \text{Integral constant} \]
\[ T_s \equiv \frac{K_i}{K_p} \]
\[ T_i \equiv \frac{K_p}{K_i} \]
\[ R \equiv \text{Thermal resistance of system} \quad T_s/\text{V}_{ss} \]
\[ \tau \equiv \text{The system time constant} \]
\[ T_{ss} \equiv \text{Steady state temperature of system} \]
\[ \text{V}_{ss} \equiv \text{Signal Voltage to power supplies} \]

By algebraic manipulation, the characteristic equation for the system transfer function listed above can be shown to be:

\[ s^2 + 2\xi \omega_n s + \omega_n^2 = 0 \]

Where:
\[ \omega_n^2 = \frac{R \cdot K_i}{\tau + R \cdot K_i} \]
\[ \xi \equiv \text{The system damping} \]
\[ \xi = \frac{R \cdot K_p + 1}{2(R \cdot K_i)^{1/2} (\tau + R \cdot K_i)} \]
\[ \psi \equiv \text{The settling time} = \frac{4}{\xi \omega_n} \]

The procedure used to calculate the PID constants is as follows:

1. The user defines a settling time and system damping, based on the desired system response.

2. The system resistance and system time constant are determined by curve fitting to the open loop system response.

3. The characteristic equation for the system is solved, resulting in solution of \( K_i \), \( T_i \), and \( T_s \).

4. The constants are input into the appropriate lines of the control program.
System includes DtoA, power supplies, heaters, and heatpipe or heatleveler

Feedback includes thermocouples, AtoD, and software
Appendix C

Derivation of the Feedforward Ramp Algorithm

The system behavior was adequately described using a first order model. The equation describing open loop behavior for a first order system is as follows.

\[ T_\ast - T_\ast = T_{ss} \left( 1 - \exp\left(-t/\tau\right) \right) \]

Where:
- \( t \) \equiv The elapsed time
- \( T_\ast \equiv \) The measured temperature at \( t \)
- \( T_\ast \equiv \) The ambient temperature at \( t = 0 \)
- \( T_{ss} \equiv \) The steady state temperature at \( t = \infty \)
- \( \tau \equiv \) The system time constant

We would like to be able to predict the amount of power needed to increase the system temperature by a specific amount. As has previously been shown, \( T_{ss} \) is proportional to the signal applied to the power supply. For this reason we may solve for \( T_{ss} \) instead of the power. The increase in temperature in a specific time period associated with a specific \( T_{ss} \) is given as follows.

\[ \Delta T = \int_{t_1}^{t_2} \frac{\delta T}{\delta t} \, dt = T_{ss} \exp\left(-t_1/\tau\right) \left[ 1 - \exp\left(-\Delta t/\tau\right) \right] \]

Where:
- \( \Delta t \equiv \) The sampling time = \( t_2 - t_1 \)

The equation listed above is expressed in terms of \( t_1 \), the time from the initiation of heating. However, the parameter
which we routinely measure is the temperature at time \( t_\text{s} \). We therefore convert to a function of measured temperature.

\[
\Delta T = (T_\text{s} + T_\text{s} - T_\text{s}) [1 - \exp(-\Delta t/\tau)]
\]

solving for \( T_\text{s} \), yields:

\[
T_\text{s} = \frac{\Delta T}{[1 - \exp(-\Delta t/\tau)] + T_\text{s} - T_\text{s}}
\]

Where:

- \( \Delta T \) = The desired temperature change
- \( T_\text{s} \) = The present value of temperature

Thus given the desired temperature change and the present value of temperature, we may calculate the appropriate signal to send to the power supply. The value for \( \Delta T \) is calculated by subtracting a theoretically calculated value desired at a future time \( t_2 \) from the present value of temperature. At present a linear ramp is used to calculate the desired temperature at time \( t_2 \).

\[
T(t) = \frac{T_\text{s}'}{t_\text{r}'} \left( t + T_\text{s} \right)
\]

Where:

- \( T_\text{s}' \) = The desired final temperature
- \( t_\text{r}' \) = The time to requested temperature
- \( T_\text{s} \) = The ambient temperature at \( t = 0 \)

Since \( \Delta T \) is not specified explicitly, it is possible to use any mathematical function to determine the desired temperature at \( t_2 \). Therefore, the algorithm could be extended to treat other thermal histories such as logarithmic or polynomial "ramps".

The values used to convert \( T_\text{s} \) to a signal voltage were determined experimentally during the open loop furnace response testing.
Appendix D

Determination of Infinite Lengths

This section outlines the procedure used to determine infinite lengths, using the criterion specified by Jasinski et. al.\textsuperscript{86}. The technique uses the effective Biot number to estimate the degree of coupling between the charge and the furnace. The effective Biot number includes the effect of the ampule and the radial heat transfer on the total heat transfer. It is suggested that the reader examine the original paper for more detail.

$$\text{Bi} \equiv \text{Biot number} = \frac{hD_{ch}}{k_{ch}}$$

Where: $h \equiv \text{Heat transfer coefficient furnace to charge}$

$$h = h_{cond} + h_{rad}$$

$D_{ch} \equiv \text{Charge diameter}$

$k_{ch} \equiv \text{Thermal conductivity of charge}$

$$h_{cond} \approx \frac{k_{g}}{r_{f}\ln(r_{f}/r_{cr})}$$

Where: $k_{g} \equiv \text{Conductivity of the ambient gas}$

$r_{f} \equiv \text{The furnace ID/2 = furnace radius}$

$r_{cr} \equiv \text{The crucible OD/2 = crucible radius}$

$$h_{rad} \approx 4F\sigma[(T_{f} + T_{ch})/2]^{3}$$

Where: $T_{f} \equiv \text{Furnace wall temperature}$

$T_{ch} \equiv \text{Charge Temperature}$

$\sigma \equiv \text{Stephan Boltzmann constant}$
\[ F = \left[ \frac{1}{\varepsilon_{ch}} + \frac{r_{ch}^2}{r_{f}^2} \right]^{-1} \left( \frac{1}{\varepsilon_r} - 1 \right)^{-1} \]

\( \varepsilon_{ch} \equiv \text{Emissivity of charge} \)
\( \varepsilon_r \equiv \text{Emissivity of furnace wall} \)

\[ Bi^* \equiv \delta Bi \left( 1 + \delta Bi \left( \frac{1}{4\gamma} - \frac{1}{2} \ln \delta \right) + \kappa \gamma + \frac{1}{(2\kappa)\delta Bi \ln \delta} \right) \]

Where:
\( \delta \equiv \frac{r_{cr}}{r_{ch}} \)
\( \kappa \equiv \frac{k_{cr}}{k_{ch}} \)
\( \gamma \equiv \delta^2 - 1 \)

\[ Bi^{**} \equiv \frac{Bi^*}{(1 + Bi^*/8)} \]

\[ L_* \equiv \frac{z_*}{(2r_{cr})^1/2} = 5/2 \left( Bi^{**} \right)^{1/2} \]

Where:
\( L_* \equiv \text{Dimensionless infinite length} \)
\( z_* \equiv \text{Infinite length} \)

Solving for \( z_* \) using the constants associated with the appropriate zone yields the infinite length for the zone.

The approximations for the heat transfer coefficients are based on the following. The conductive heat transfer to the charge is limited, therefore dominated, by conduction through the gas phase since the thermal conductivity of the gas is 2 orders of magnitude lower than that for the crucible. The approximate heat transfer coefficient for radiation follows Rohsenow and Choi\(^\text{32}\).
Appendix E

Selected Thermophysical Properties

E.1 For CdTe

Glazov et. al.\textsuperscript{13,3}
coefficient of linear expansion = \(4.99 \times 10^{-6}\)
Density of solid @ \(T_{\text{melt}}\) = 5.690 g/cm\(^3\)
Density of liquid @ \(T_{\text{melt}}\) = 5.670 g/cm\(^3\)

Glazov et. al.\textsuperscript{13,4}
Viscosity = 0.330 - 0.435 centistokes depends on \(T\) also
function of composition 0.413 @ 1097°C and stoichiometric composition.
Conductivity liquid = 45 - 168 \(\Omega^{-1}\)cm\(^{-1}\) increases with
increasing temperature = 96 \(\Omega^{-1}\)cm\(^{-1}\) @ 1100°C

Rud and Sanin\textsuperscript{9,1}
Diffusivity of liquid: Function of stoichiometry
High \(D_{\text{c,i}}\) \(\approx\) \(1 \times 10^{-5}\) cm\(^2\)/sec
Low \(D_{\text{c,i}}\) \(\approx\) \(8 \times 10^{-5}\) cm\(^2\)/sec
Average \(\approx\) \(3.7 \times 10^{-5}\) cm\(^2\)/sec

Ratio electrical conductivity liquid/solid \(\approx\) 4.5
Conductivity of liquid obeys \(\sigma_i = \sigma_0 \exp(-0.85\ \text{eV/kT})\)

Kulwicki\textsuperscript{14,8}
Heat of fusion 12.0 \pm 1.9 Kcal/gm-mole

From Thermophysical properties of matter:\textsuperscript{15,3}
$C_p = \text{Specific heat follows } AT + b = \ln C_p \text{ where } A = 0.000244; \ b = -2.951127; \ R^2 = 0.999638 \text{ for data obtained in the 300 - } 1000^\circ K) \text{ extrapolated to } 1092^\circ C = 7.294 \times 10^{-2} \text{ cal/g}^\circ K^{1.56}$

Emittance: @ 75 µm 0.437-0.555 $^{137}$
        @ 44.5 µm 0.428

Sen et. al.$^{146}$

Thermal diffusivity of Solid 0.010 cm$^2$/sec
Thermal diffusivity of Melt 0.012 cm$^2$/sec
Appendix F

Determination of the Rotational Relation between Crystals

The technique used to determine the rotational matrix between two adjacent grains is presented briefly in this section.

From the Laue pattern we may identify the direction cosines of the center and north poles. With this data we may uniquely specify the orientation of the crystal in space. By taking the cross product of the Center and North poles we may determine a third orthogonal axis which defines a space. It may be shown that the interplanar angle of two planes with normals \([h_1 k_1 l_1]\) and \([h_2 k_2 l_2]\) can be expressed as:

\[
\cos \phi = \frac{d_1 d_2}{V^2} \left[ S_{11} h_1 h_2 + S_{22} k_1 k_2 + S_{33} l_1 l_2 + S_{23} (k_1 l_2 + k_2 l_1) + S_{13} (l_1 h_2 + l_2 h_1) + S_{12} (h_1 k_2 + h_2 k_1) \right]
\]

Where:

\[
\frac{1}{d^2} = \frac{1}{V^2} \left[ S_{11} h^2 + S_{22} k^2 + S_{33} l^2 + 2(S_{12} hk + S_{23} kl + S_{13} hl) \right]
\]

\[
V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma}
\]

\[
S_{11} = b^2 c^2 \sin^2 \alpha
\]

\[
S_{22} = a^2 c^2 \sin^2 \beta
\]

\[
S_{33} = a^2 b^2 \sin^2 \gamma
\]

\[
S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma)
\]

\[
S_{23} = a^2 b c (\cos \beta \cos \gamma - \cos \alpha)
\]

\[
S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta)
\]

\[a,b,c\] are the lengths of the crystallographic axes.
α, β, γ are the angles between the crystallographic axes
In the case of cubic crystals the simplifications a = b = c and α = β = γ = 90° can be made.

Using the above equation we may calculate a 3x3 matrix which contains the interplanar angle between the center, north, and east and the [100], [010], and [001]. Repeating the process for the second grain, without disturbing the orientation of the first, we obtain a similar matrix. Since the north, center, and east are invariant between the two grains we may find the relative angle between the [100], [010], and [001]. From the differences in the <100> directions a rotational transform matrix can be constructed. By multiplying this rotation transformation matrix by the 24 symmetry operations for cubic crystals we obtain a complete description of the relation between the two grains. Each of the 24 rotation matrices is converted to an axis angle pair using the following relationships:

\[ h_\ast = \frac{[M_{31} - M_{13}]}{2 \sin \theta} \]
\[ k_\ast = \frac{[M_{12} - M_{21}]}{2 \sin \theta} \]
\[ l_\ast = \frac{[M_{23} - M_{32}]}{2 \sin \theta} \]
\[ \cos \theta = \frac{1}{2} [M_{11} + M_{22} + M_{33} - 1] \]

Where:
M's are the matrix elements
\( h_\ast, k_\ast, l_\ast \) are the direction cosines of the rotation axis
\( \theta \) = The rotation angle

Using the minimum rotation angle convention, we may identify an axis angle pair which describes the relationship between the two grains. Comparing the experimentally determined value to published data for special high
symmetry boundaries allows us to determine if the two grains are related in a high order twin.

Given an axis angle description relating two crystals, we may generate the rotational transformation matrix which maps one crystal into the other.

\[ R_{i,k} = \delta_{i,k} \cos \theta + c_i c_k (1 - \cos \theta) + c_k \sin \theta \]

Where:
- \( R_{i,k} \equiv \) Rotation transformation matrix element
- \( c_i \equiv \) The direction cosines of the rotation axis
- \( \theta \equiv \) The rotation angle
- \( \delta_{i,k} \equiv \) Delta function, i.e. 0 when \( i \neq k \), 1 when \( i = k \)

\[
c_{i,k} = \begin{pmatrix}
0 & -c_3 & c_2 \\
c_3 & 0 & -c_1 \\
-c_2 & c_1 & 0
\end{pmatrix}
\]
Appendix G

High Order Twinning

High order twins can be considered grain boundaries since they are incoherent planar defects. The grains are however related in specific angular relationships which is a result of their formation mechanism. Figure G.1 is a graphic representation of a second order twin. The formation mechanism can be understood if we recall that there are four physically distinct twins possible in the zincblende structure generated by a rotation of 180° about any of the \( <111> \)'s. If a twin intersects another twin which is a rotation about a different \( [111] \), a second order twin results. Although each of the component twins is coherent with the parent grain, the resultant second order twin is not since rotation about a different twin axis will not result in atomic registry between the intersecting first order twins. A third order twin can be generated by intersection of a second order twin with a different first order twin. The process can be repeated to generate a \( n^{th} \) order twin. Since these defects are generated by interaction of twins, they are expected to be prevalent in systems with low twin plane energies. Polycrystalline growth by high order twinning has been observed in semiconductors with much higher stacking fault energies than CdTe\(^{159}\), such behavior was also observed in this study.

The rotation angle-axis pair for high order twins has been published up to a fourth order twin in Grain Boundary Structure and Kinetics\(^{40}\). The nomenclature used in this source is however based on the alternative \( \Sigma \) \( n \) or coincident
site lattice nomenclature. The boundaries are expressed in terms of the reciprocal of the fraction of lattice points in common between the two structures. A detailed description of this convention is beyond the scope of this work, however one may translate from the high order twin nomenclature to the $\Sigma n$ nomenclature quite easily. A $\Sigma 3$ boundary is a first order twin, while a fourth order twin is a $\Sigma 81$. The general expression for an $n^{th}$ order twin is $\Sigma 3^n$. Gottstein\textsuperscript{160} has published the axis-angle pairs for up to a seventh order twin, however approximations are involved.
Figure G.1: Schematic representation of a second order twin

Second Order (Incoherent)
Twin Boundary

(T₁₂)

Twinned Crystal
(Coherent)

(T₂)

Twinned Crystal
(Coherent)

(T₁)

Parent Crystal
(P)

Four Crystallographically Equivalent Twinning Operations are Possible in ZnSBlende
Designated T₁ - T₄
Appendix H

Measurement of Temperature Profiles

Temperature profiles were used to characterize the furnace. All measurements were made using a 0.16 cm diameter, 91.44 cm long, inconel sheathed, calibrated, type K thermocouple. The thermocouple was placed in a 2x3 mm quartz tube to keep it aligned and insure the positional measurements were reproducible. Since in general the presents of a charge effects the temperature profile, a number of configurations were examined. These include:

1. An empty furnace with an Ar gas ambient

2. An empty furnace with a roughing pump vacuum ~150 microns

3. The furnace with an evacuated bicylindrical thermal probe (EBTP) installed. The EBTP vacuum was better than 1x10^-7 torr. See Figure H.1

4. The furnace with a specially designed model charge installed. See Figure H.2

In order to determine the effect of having a charge in the furnace cavity, a specially designed model charge was constructed. The model charge consisted of a 16 x 20 mm quartz ampule with a 5 x 8 mm quartz tube centered inside it. CdTe was placed such that it filled the volume between the two quartz tubes. The charge was placed so as to be traversing the gradient zone while having an infinite length in each active zone. A temperature profile of the central
ampule cavity was then obtained. The profiles were compared to an empty furnace with Ar and an empty furnace with vacuum. The results of these experiments are presented in figure H.3.

The empty furnace with Ar gave a profile which was considerably different from the one obtained using the model charge, probably due to enhanced heat transfer by convection of the Ar gas. Measuring the profile in an evacuated furnace yielded results similar to those obtained using the model charge, but had deleterious effects on the unsheathed PtRh thermocouples and heaters, leading to premature failure of these components. In particular, the PtRh thermocouples would not survive even short exposures to high temperature. Examining them after the run revealed they had melted in localized regions, suggesting alloying had occurred. Temperature profiles were therefore routinely obtained using the EBTP. The design of the EBTP is very similar to the actual growth ampules. Indeed a comparison of the profile obtained using it compared to the model charge yielded similar results figure 4.19.
Figure H.1: Evacuated bicylindrical thermal probe

Top of Ampule
84 cm nominal

Temperature profile is taken by sliding a calibrated thermocouple in the central ampule cavity

Outer ampule
16x20 mm nominal

Inner ampule
5x8 mm nominal

Bottom Seal
8 cm nominal

0 cm

Upper Heatpipe
Insulation
Ni Heat Leveler
Gradient Zone
Lower Heatpipe
Figure H.2: Model charge used for temperature profiling

Top of Ampule
84 cm nominal

CdTe Charge
43 cm nominal

Outer ampule
18x20 mm
nominal

Inner ampule
5x3 mm
nominal

Quartz Seal
8 cm nominal

0 cm

Upper Heatpipe

Insulation

Ni Heat Leveler

Gradient Zone

Lower Heatpipe
Figure H.3: Temperature profiles measured using different furnace ambients

Distance Above Support Shaft (cm)

Ar Gas
Vacuum
Model Charge

Celsius

800 900 1000 1100 1200 1300
Appendix I

The Furnace Control Program

5 REM Copyright (C) James S. Nakos 1985,1986,1987 All rights reserved.
10 ON ERROR GOTO 530
15 COMMON OUTNAME$,NUMBER,SKIP
20 REM ******** This section defines the arrays used **********************
30 REM
40 DIM DERVHIS(3,15),TEMP(15),DERIV(15),INTEG(15),TAURES(2),TAU(2),
50 DIM EROE(15),ELAPSE(15),KP(2),INTE(2),DERV(2),PROP(2),SIGNAL(2),
60 DIM TAMBIENT(2),MAXSIG(2),TIMETOT(2),TRATE(2),SYRS(2),SYSOFF(2),
70 DIM EXCONST(2),TO(5),T1(5),T2(5),T3(5),RAMPFLAG(2),RAMPPOJ(2),
80 DIM TIMESTART(3),AVGDELT(2),APP(2),PROCESS(50,4),DOWN(2),SWITCH(2)
90 DIM OLDSIG(2),NEWSIG(2),RATIOFLG(2),AMPFACT(2),VOLTFACT(2),VOLT(2),
100 DIM SIGERR(2),OLDSIGER(2),BLOWFUSE(2),MAXVOLT(2),OVERTEMP(2),
110 REM ******** This section defines the constants***********************
120 REM
130 REM
140 REM SAMPBR= 20 : LASTPOS = 0 : PASTPOS = 0 : FILENUM = 0:BEGINC=1:
150 REM EMERG=0
160 HOURS=0:MIN=0:SECONDS=0:MARKSTR=0:DAYs=0:MARKNUM=0:MARKON=0:
170 ALTRATE=2:ALTSIG=2.307:MARKINT=18000:MARKLEN=1800:MARKS=5:
180 MAXRATE=127:
190 MARKLEN=INT(MARKLEN/SAMPBRAT)
200 RAMPFLAG(0)=0 : RAMPFLAG(1)=0 : RAMPFLAG(2)=0
210 RAMPPOJ(0)=5:RAMPPOJ(1)=8:RAMPPOJ(2)=5
220 LOW=0:PROC=0:TOLLEN=0
230 ZONELAB$(0)="BOTTOM":ZONELAB$(1)="MIDDLE":ZONELAB$(2)="TOP"
240 PFLAG=-1 : PLOT=0 : PTFLAG=0 : PFACTOR=1:POFFSET=0:PCENTER=0
250 SAVPOS=0:MAXTIME = -1:LOWRATE=0:LOWSIG=0
260 MAXSIG=4.999:MAXSIGM=4.999:MAXSIGT=9.9799999
270 BOTT=3000:MAID=3000:TOPTAU=3000
280 BOTR=277:MIDR=405:TOPR=145
290 BOTT=98:MID=20:TOP=205
300 MAXTEMP=1050:MAXTEMPM=1205:MAXTEMP=1000:MAXTEMP=1225
310 MAXVOLT=80 : MAXVOLT1=80 : MAXVOLT2=60
320 OLDSIGER=0.1 : OLDSIGER1=0.1 : OLDSIGER2=0.1
330 BLOWFUSE=0 : BLOWFUSE1=0 : BLOWFUSE2=0
340 OLDSIG=0.1:OLDSIG1=0.1:OLDSIG2=0.1

- 216 -
NEWSIG(0)=1:NEWSIG(1)=1:NEWSIG(2)=1
RATIOFLG(0)=0:RATIOFLG(1)=0:RATIOFLG(2)=0
APP(0)=60:APP(1)=39:APP(2)=60
DOWN(0)=0:DOWN(1)=0:DOWN(2)=0
KP(0)=20:KP(1)=13:KP(2)=30
TAUD(0)=.01:TAUD(1)=.01:TAUD(2)=.01
TAUI(0)=15000:TAUI(1)=25000:TAUI(2)=15000
MAXARRAY=100
TMP0=0:TMPA0=0:TMPB0=0:TMPC0=0:TMPD0=0
TMP1=0:TMPA1=0:TMPB1=0:TMPC1=0:TMPD1=0
TMP2=0:TMPA2=0:TMPB2=0:TMPC2=0:TMPD2=0
TMP3=0:TMPA3=0:TMPB3=0:TMPC3=0:TMPD3=0
TEMP4=0:TEMP5=0
AMPO=0:AMP1=0:AMP2=0
TACHVOLT=0
VOLTO=0:VOLT1=0:VOLT2=0
OVERTEMP(0)=0:OVERTEMP(1)=0:OVERTEMP(2)=0
REM ** The next section checks if data files have been saved ***
NAME "growth.par" AS "CRAL1."
NAME "cral1." AS "growth.par"
IF ERR=58 THEN PRINT "Save or delete old data files.":NAME "cral1." AS "growth.par"
ON ERROR GOTO 0
OPEN "I",#1,"growth.par"
PN=0
IF EOF(1) THEN GOTO 620
INPUT #1,
PROCESS(PN,0),PROCESS(PN,1),PROCESS(PN,2),PROCESS(PN,3),PROCESS(PN,4)
PRINT
PROCESS(PN,0),PROCESS(PN,1),PROCESS(PN,2),PROCESS(PN,3),PROCESS(PN,4)
PN = PN+1
GOTO 570
PROCESS(PN,0) = -1
CLOSE #1
REM ****** The next line determines which zone should be plotted **
PLOT=1
PRINT "Would you like to automatically convert the data after completion?"
CONVDATE$ = INPUT$(1)
IF CONVDATE$ = "n" OR CONVDATE$ = "N" THEN GOTO 660
PRINT "What rootname should be used for the converted files?"
LINE INPUT "up to 8 characters":CONVNAME$
INPUT "How many points should be skipped":CONVSkip
CALL INIT
REM
TAU(0)=BOTTAU:TAU(1)=MIDTAU:TAU(2)=TOPTAU
SYSR(0)=BOTR:SYSR(1)=MIDR:SYSR(2)=TOPR
SYSOFF(0)=BOTTFF:SYSOFF(1)=MIDFF:SYSOFF(2)=TOPFF
MAXSIG(0)=MAXSIGB:MAXSIG(1)=MAXSIG:MAXSIG(2)=MAXSIGT
MAXTEMP(0)=MAXTEMPB:MAXTEMP(1)=MAXTEMPM:MAXTEMP(2)=MAXTEMPT:
MAXTEMP(3)=MAXTEMPS
FFACT=1.43
740 AMPFACT(0) = -10: AMPFACT(1) = -1/.025: AMPFACT(2) = 1/.025
750 VOLTFACT(0) = 129/1.4*FFACT: VOLTFACT(1) = 134/1.4*FFACT: VOLTFACT(2) = -135/1.9*FFACT
760 TACHFACT = 239/21
770 REM ******* Declaration of I/O names ............................
775 REM ************************************************************************
780 REM ************************************************************************
780 REM ********************************************************************************
800 CALL IONAME( "lowamp", 1, 0, 14)
810 CALL IONAME( "midamp", 1, 1, 14)
820 CALL IONAME( "topamp", 1, 2, 14)
830 CALL IONAME( "tach", 1, 3, 14)
840 CALL IONAME( "lowvolt", 1, 4, 14)
850 CALL IONAME( "midvolt", 1, 5, 14)
860 CALL IONAME( "topvolt", 1, 6, 14)
870 CALL IONAME( "lowps", 10, 1, 13)
880 CALL IONAME( "midps", 10, 1, 14)
890 CALL IONAME( "topps", 10, 1, 15)
900 CALL IONAME( "temp0", 3, 0, 14, 2)
910 CALL IONAME( "temp1", 3, 1, 14, 2)
920 CALL IONAME( "temp2", 3, 2, 14, 2)
930 CALL IONAME( "temp3", 3, 3, 14, 2)
940 CALL IONAME( "temp4", 3, 4, 14, 2)
950 CALL IONAME( "temp5", 3, 5, 14, 2)
960 CALL IONAME( "tempref", 3, 32, 14)
970 CALL IONAME( "botout", 5, 0)
980 CALL IONAME( "midout", 5, 1)
990 CALL IONAME( "topout", 5, 2)
1000 CALL IONAME( "Transout", 5, 3)
1010 CALL IONAME( "plotter", 5, 4)
1020 REM ****** The next line turns on the powersupplies ***********
1030 GOSUB 4780
1040 REM ************************************************************************
1050 REM ************************************************************************
1050 REM ************************************************************************
1060 REM ************************************************************************
1070 REM ************************************************************************
1080 CALL INTON("samprate%" , "sec")
1090 CALL ANIN( "CrA1%" , maxarray, "tempref,temp0,temp0,temp0,temp0,temp0,temp1,temp1,temp1,temp1,temp4,temp5", 1, -1, "CrA1temp")
1100 CALL ANIN( "CrA2%" , maxarray, "tempref,temp2,temp2,temp2,temp2,temp2,temp3,temp3,temp3,temp3,temp3", 1, -1, "CrA2temp")
1110 CALL ANIN( "pow%" , maxarray, "lowamp,midamp,topamp,tach,lowvolt,midvolt,topvolt", 1, -1, "powarray")
1120 CALL ARLASTP("CrA2%", LASTPOS)
1130 DELTAPOS = ABS(LASTPOS-PASTPOS)
1140 IF DELTAPOS = 0 THEN GOTO 1120
1150 PASTPOS = LASTPOS
1160 IF LASTPOS <> MAXARRAY-DELTAPOS THEN 1190 ELSE 1420
1170 REM ************************************************************************
1180 REM ************************************************************************
1190 REM ************************************************************************
1200 REM ************************************************************************
1210 FILENUM = FILENUM + 1
1220 NUM$ = STR$(FILENUM)
1230 NUM$ = RIGHT$(NUM$,LEN(NUM$)-1)
1240 FUN1$ = "Cr1" + NUM$
1250 FUN2$ = "Cr1" + NUM$
1260 FUN3$ = "pow" + NUM$
1270 PRINT FUN1$, FUN2$
1280 CALL INTOFF
1290 CALL ARSAVE("Cr11", fun1$)
1300 CALL ARSAVE("Cr12", fun2$)
1310 CALL ARSAVE("pow", fun3$)
1320 CALL BACKCLEAR
1330 CALL ARDEL("Cr11")
1340 CALL ARDEL("Cr12")
1350 CALL ARDEL("pow")
1360 SAVEPOS = SAVEPOS + LASTPOS
1370 LASTPOS = 0 : PASTPOS = 0
1380 IF EMOFOFF=1 THEN RETURN
1390 GOTO 1080
1400 REM ************************************************************************
1410 REM                         **************
1420 REM *** This section obtains temperatures from the bkgnd array ***
1430 REM  ****************************
1440 CALL ARGETVAL("Cr11", lastpos,2,tmp0,11)
1450 CALL ARGETVAL("Cr11", lastpos,3,tmpa0,11)
1460 CALL ARGETVAL("Cr11", lastpos,4,tmpb0,11)
1470 CALL ARGETVAL("Cr11", lastpos,5,tmpc0,11)
1480 CALL ARGETVAL("Cr11", lastpos,6,tmpd0,11)
1490 CALL ARGETVAL("Cr11", lastpos,7,tmp1,11)
1500 CALL ARGETVAL("Cr11", lastpos,8,tmpa1,11)
1510 CALL ARGETVAL("Cr11", lastpos,9,tmpb1,11)
1520 CALL ARGETVAL("Cr11", lastpos,10,tmpc1,11)
1530 CALL ARGETVAL("Cr11", lastpos,11,tmpd1,11)
1540 CALL ARGETVAL("Cr11", lastpos,12,temp4,11)
1550 CALL ARGETVAL("Cr11", lastpos,13,temp5,11)
1560 CALL ARGETVAL("Cr12", lastpos,2,tmp2,11)
1570 CALL ARGETVAL("Cr12", lastpos,3,tmpa2,11)
1580 CALL ARGETVAL("Cr12", lastpos,4,tmpb2,11)
1590 CALL ARGETVAL("Cr12", lastpos,5,tmpc2,11)
1600 CALL ARGETVAL("Cr12", lastpos,6,tmpd2,11)
1610 CALL ARGETVAL("Cr12", lastpos,7,tmp3,11)
1620 CALL ARGETVAL("Cr12", lastpos,8,tmpa3,11)
1630 CALL ARGETVAL("Cr12", lastpos,9,tmpb3,11)
1640 CALL ARGETVAL("Cr12", lastpos,10,tmpc3,11)
1650 CALL ARGETVAL("Cr12", lastpos,11,tmpd3,11)
1660 CALL ARGETVAL("pow", lastpos,1,amp0,0)
1670 CALL ARGETVAL("pow", lastpos,2,amp1,0)
1680 CALL ARGETVAL("pow", lastpos,3,amp2,0)
1690 CALL ARGETVAL("pow", lastpos,4,tachvolt,0)
1700 CALL ARGETVAL("pow", lastpos,5,volt0,0)
1710 CALL ARGETVAL("pow", lastpos,6,volt1,0)
1720 CALL ARGETVAL("pow", lastpos,7,volt2,0)
1730 REM **********************************************************************
1740 REM ******* THERMOCOUPLE ASSIGNMENTS ****************************
1750 REM ************************************************************************
1760 AMP(0)=AMP0*AMPFAC(0):AMP(1)=AMP1*AMPFAC(1):AMP(2)=AMP2*AMPFAC(2)
1770 VOLT(0)=VOLTO*VOLTFAC(0):VOLT(1)=VOLTO*VOLTFAC(1):VOLT(2)=
VOLTO*VOLTFAC(2)
1780 TACHVOLT=TACHVOLT*TACHFACT
1790 TO(0)=TMP0:TO(1)=TMPA0:TO(2)=TMPB0:TO(3)=TMPC0:TO(4)=TMPD0
1800 T1(0)=TMP1:1(T1(1)=TMPA1:T1(2)=TMPB1:T1(3)=TMPC1:T1(4)=TMPD1
1810 T2(0)=TMP2:T2(1)=TMPA2:T2(2)=TMPB2:T2(3)=TMPC2:T2(4)=TMPD2
1820 T3(0)=TMP3:T3(1)=TMPA3:T3(2)=TMPB3:T3(3)=TMPC3:T3(4)=TMPD3
1830 MAXD=TO(D):MINO=TO(0)
1840 MAX1=T1(0):MIN1=T1(0)
1850 MAX2=T2(D):MIN2=T2(0)
1860 MAX3=T3(D):MIN3=T3(0)
1870 TOTOT = TO(0)
1880 T1TOT = T1(0)
1890 T2TOT = T2(0)
1900 T3TOT = T3(0)
1910 FOR N = 1 TO 4
1920 IF TO(N) > MAXD THEN MAXD = TO(N)
1930 IF T1(N) > MAX1 THEN MAX1 = T1(N)
1940 IF T2(N) > MAX2 THEN MAX2 = T2(N)
1950 IF T3(N) > MAX3 THEN MAX3 = T3(N)
1960 IF TO(N) < MINO THEN MINO = TO(N)
1970 IF T1(N) < MIN1 THEN MIN1 = T1(N)
1980 IF T2(N) < MIN2 THEN MIN2 = T2(N)
1990 IF T3(N) < MIN3 THEN MIN3 = T3(N)
2000 TOTOT = TOTOT + TO(N)
2010 T1TOT = T1TOT + T1(N)
2020 T2TOT = T2TOT + T2(N)
2030 T3TOT = T3TOT + T3(N)
2040 NEXT N
2050 T0AVG = (TOTOT-MAXD-MINO)/3
2060 T1AVG = (T1TOT-MAX1-MIN1)/3
2070 T2AVG = (T2TOT-MAX2-MIN2)/3
2080 T3AVG = (T3TOT-MAX3-MIN3)/3
2090 REM ************************************************************************
2100 REM ************************************************************************
2110 REM ******* The next section assigns thermocouples to each zone **
2120 REM ************************************************************************
2130 TEMP(0) = T0AVG : IF TEMP(0) > MAXTEMP(0) THEN GOTO 5270
2140 TEMP(1) = T1AVG : IF TEMP(1) > MAXTEMP(1) THEN GOTO 5270
2150 TEMP(2) = T2AVG : IF TEMP(2) > MAXTEMP(2) THEN GOTO 5270
2160 SAFETY(2) = T3AVG
2170 SAFETY(0)=TEMP4 : SAFETY(1)=TEMP5
2180 GOSUB 7000
2200 REM ************************************************************************
2210 REM ******* The next line gets the growth parameters from the
process ****
2220 IF (ELAPSE=>PROCESS(PROC,0))AND(LOWER<1)AND(PROCESS(PROC,0)=>0)
THEN GOTO 5690
2230 REM ************************************************************************
2240 REM
2250 REM ******************** The P.I.D. portion of the program ********************
2260 REM
2270 ERR = SET - TEMP
2280 ERR1 = SET1 - TEMP1
2290 ERR2 = SET2 - TEMP2
2300 REM ***************************************************************************
2310 REM
2320 REM The next section sets up a temperature history for the derivative
2330 REM
2340 TC = 0 : GOSUB 3190
2350 TC = 1 : GOSUB 3190
2360 TC = 2 : GOSUB 3190
2370 IF LASTPOS <= 4 THEN 2450
2380 REM ***************************************************************************
2390 REM
2400 REM The next section actually calculates the derivative (3pt backward)
2410 REM
2420 TC = 0 : GOSUB 3250
2430 TC = 1 : GOSUB 3250
2440 TC = 2 : GOSUB 3250
2450 TPOS = SAVEPOS + LASTPOS
2460 ELAPSE = TPOS * SAMPRATE%
2470 IF LOWER (<1 THEN GOTO 2570
2480 CALL CLOCKREAD(hours, min, sec)
2490 MTIME = HOURS*3600+MIN*60+SEC
2500 IF MARKSTRT = 0 THEN OLDMARK = MTIME ; MARKSTRT=1
2510 IF (MTIME < OLDMARK AND NEWDAY = 0) THEN DAYS = DAYS+1 : NEWDAY = 1
2520 IF MTIME > OLDMARK THEN NEWDAY = 0
2530 MARKTIME = DAYS * 86400 + MTIME - OLDMARK
2540 IF (MARKTIME >= MARKINT+ MARKNUM * MARKINT AND MARKINT>0) THEN GOSUB 6270
2550 TOTLEN = TOTLEN + DELTAPOS * SAMPRATE% / ABS(LOWRATE) / 3600
2560 IF TOTLEN < MAXLEN THEN GOSUB 5490
2570 IF (ELAPSE > MAXTIME AND MAXTIME > 0) THEN GOTO 5430
2580 REM ***************************************************************************
2590 REM
2600 REM This section obtains the heater signals for each zone
2610 REM
2620 FOR Z = 0 TO 2
2630 IF DOWN(Z)=1 THEN GOTO 2690
2640 IF (TEMP(Z) < SET(Z) - SET(Z)/APP(Z)) AND (RAMPFLG(Z)=0) THEN GOSUB 4860: GOTO 2740
2650 IF SWITCH(Z)=1 THEN GOTO 2680
2660 INTEG(Z) = (SIGNAL(Z) / MAXSIG(Z) - KP(Z) * (ERROR(Z) / SET(Z) - TAU(Z) * DERIV(Z))) * TAU(Z) / KP(Z)
2670 SWITCH(Z) = 1
2680 GOSUB 4170

- 221 -
2690 IF (TEMP(Z)>SET(Z)+SET(Z)/APP(Z)) AND (RAMPFLAG(Z)=0) THEN GOSUB 4860: GOTO 2740
2700 IF SWITCH(Z)=1 THEN GOTO 2730
2710 INTEG(Z)=(SIGNAL(Z)/MAXSIG(Z)-KP(Z)*ERROR(Z)/SET(Z)-TAUD(Z)*
DERIV(Z))/TAUZ(KP/Z)
2720 SWITCH(Z)=1
2730 GOSUB 4170
2740 NEXT Z
2750 REM *********************************************
2760 REM This section associates the signal array with the appropriate zone ***
2770 REM *********************************************
2780 SIGNALB = SIGNAL(0)
2790 SIGNALM = SIGNAL(1)
2800 SIGNALT = SIGNAL(2)
2810 SIGNALP = (TEMP(PLOT)-POFFSET)*9.998/1300 * PFACTOR + PCENTER
2820 REM *********************************************
2830 REM ********** This section clamps the output voltage *************
2840 REM *********************************************
2845 GOSUB 6710
2850 REM check fuses GOSUB 6480
2860 IF SIGNALB < 0 THEN SIGNALB = 0
2870 IF SIGNALB > MAXSIGB THEN SIGNALB = MAXSIGB
2880 IF SIGNALM < 0 THEN SIGNALM = 0
2890 IF SIGNALM > MAXSIGM THEN SIGNALM = MAXSIGM
2900 IF SIGNALT < 0 THEN SIGNALT = 0
2910 IF SIGNALT > MAXSIGT THEN SIGNALT = MAXSIGT
2920 IF LOWSIG < -3 THEN LOWRATE=LOWRATE*-3/LOWSIG : LOWSIG = -3
2930 IF LOWSIG > 3 THEN LOWRATE=LOWRATE*3/LOWSIG : LOWSIG = 3
2940 CALL ANWRITE("b10ut",signalb,0)
2950 CALL ANWRITE("midout",s SIGNALM,0)
2960 CALL ANWRITE("topout",signalT,0)
2970 CALL ANWRITE("Transout",lowSig,0)
2980 CALL ANWRITE("plotter",signalP,0)
2990 REM ********** The next line prints the temperatures to the screen
3000 IF PFLAG = 1 THEN GOSUB 4310
3010 REM IF (ELAPSE => PROCESS(PROC,0)) AND (LOWER <= 1) THEN GOTO 5020
3020 REM ********** The next line changes the growth parameters
3030 T$ = INKEY$: IF T$ = "s" THEN GOSUB 3480
3040 REM ********** The next line changes the system constants ********
3050 IF T$="c" THEN GOSUB 3880
3060 REM ********** The next line allows a different zone to be plotted
*********
3070 IF T$ ="p" THEN GOSUB 4060
3075 IF T$ ="h" THEN GOSUB 6880
3080 IF T$ ="l" THEN GOSUB 3710
3090 IF T$="d" THEN PFLAG=-1*PFLAG
3100 IF T$ = "m" THEN GOSUB 5350
3110 IF T$ ="e" THEN CLS
3120 IF T$ ="t" THEN GOSUB 5580
3130 IF T$ ="v" THEN GOSUB 6020
3140 IF T$ = "r" THEN GOSUB 6140

- 222 -
GOTO 1120
REM ***************************************************
REM ***************************************************
REM ***************************************************
REM ***** Real time derivative subroutine (3 term backward difference) **
DERVHIS(0,TCOUPLE) = DERVHIS(1,TCOUPLE)
DERVHIS(1,TCOUPLE) = DERVHIS(2,TCOUPLE)
DERVHIS(2,TCOUPLE) = DERVHIS(3,TCOUPLE)
DERVHIS(3,TCOUPLE) = TEMP(TCOUPLE)
RETURN
D=11*DERVHIS(3,TCOUPLE)-18*DERVHIS(2,TCOUPLE)+9*DERVHIS(1,TCOUPLE)-
2*DERVHIS(0,TCOUPLE)
DERIV(TCOUPLE) = D/6 * 1/(DELTAPOS * SAMPRATE%)
RETURN
REM ***************************************************
REM ***************************************************
REM ***** This section performs real time integration ***********
INTEG(TCOUPLE) = INTEG(TCOUPLE) + EROR(TCOUPLE)
RETURN
REM ***************************************************
REM ***************************************************
REM ***** This section inputs set points ***********
FOR Z = 0 TO 2
GOSUB 3500
NEXT Z
BEGIN = 0
LASTPOS=0:PASTPOS=0
CALL INTOFF
CALL ARDEL('"CrAl11"')
CALL ARDEL('"PtRh1"')
CALL BACKCLEAR
GOTO 1080
CLS
INPUT"Which zone would you like to change '0=BOTTOM, 1=MIDDLE, 2=TOP':";Z
IF(Z=0) AND (Z<=2) THEN 3530
CLS
PRINT "ERROR......Zone must be between 0 - 2":RETURN
CLS
SETLABEL$ = "Desired temperature of "+ZONELAB$(Z)+" zone"
TIMESTART(Z) = TOTPOS*SAMPRATE%
LOCATE 5,1
PRINT SETLABEL$:
INPUT SET(Z)
IF SET(Z)=0 THEN SET(Z)=1
GOSUB 5180
IF EFLAG = 1 GOTO 3560
LOCATE 7,1
3630 INPUT "Approximately when should the temperature be reached (sec)":
3635 TIMET0T(Z)
3640 RAMPFLAG(Z)=0
3650 IF TEMP(Z)>SET(Z) THEN DOWN(Z)=1:CALCSIG=(SET(Z)+SET(Z)/APP(Z)-
3655 SYSOFF(Z))/SYSR(Z) ELSE CALCSIG=(SET(Z)-SET(Z)/APP(Z)-
3660 SYSOFF(Z))/SYSR(Z):DOWN(Z)=0
3665 DERIV(Z)=0:INTEG(Z)= CALCSIG/MAKSIG(Z)*TAUI(Z)/KP(Z)
3670 PROP(Z)=0:DERIV(Z)=0:INTEG(Z)=0
3680 GOSUB 5030
3690 IF EFLAG = 1 GOTO 3560
3700 RETURN
3710 REM ************************************************************
3720 REM **** This section enters the lowering rate and other data ****
3730 REM *******************************************************
3740 CLS
3750 TIMESTART(Z) = ELAPSE
3760 LOCATE 5,1
3770 INPUT "Ampule lowering rate (cm/hr)";LOWRATE
3780 IF EFLAG = 1 THEN GOTO 3740
3790 LOCATE 7,1
3800 INPUT "What is the desired length of crystal (cm)";MAXLEN
3810 IF EFLAG = 1 THEN GOTO 3790
3820 LOCATE 9,1
3830 INPUT "What is the gear ratio";GEARRAT
3840 IF EFLAG = 1 THEN GOTO 3820
3850 LOWSIG = -1 * LOWRATE* 2.778* .4153 *GEARRAT/50
3860 LOWER=1
3870 RETURN
3880 REM *******************************************************
3890 REM ************************************************************
3900 REM **** This subroutine changes the constants for the system ****
3910 REM *******************************************************
3920 CLS
3930 INPUT "Which zone do you want to change 0=Bottom,1=Middle,2=Top":
3940 IF (ZONE=0) AND (ZONE=2) THEN 3970
3950 LOCATE 25,1
3960 PRINT "ERROR Zone must be between 0-2":RETURN
3970 OLDTAUI = TAUI(ZONE)
3980 OLDPK=KP(ZONE)
3990 INPUT "What is the new value for the proportional constant":
4000 IF (ZONE=0) THEN 4005
4005 PRINT "ERROR Zone must be between 0-2":RETURN
4010 INPUT "What is the new derivative time constant";TAUD(ZONE)
4020 INPUT "What is the new integral time constant";TAUI(ZONE)
4030 INTEG(ZONE) = TAUI(ZONE)/OLDTAUI*OLDPK/KP(ZONE)*INTEG(ZONE)
4040 CLS
4050 RETURN
4060 REM ************************************************************
4070 REM **** This section selects which zone should be plotted ****
4080 REM *******************************************************
4090 INPUT "For which zone should the temperature be plotted":PLOT
4100 IF (PLOT=>0) AND (PLOT<=3) THEN 4130
4110 LOCATE 25.1
4120 PRINT "ERROR Zone must be between 0-3 default to 1":PLOT=1:
            RETURN

4130 CLS
4140 RETURN
4150 REM *****************************************
4160 REM *****************************************
4170 REM ***** This section determines the heater signals ******
4180 REM *****************************************
4190 RAMPFLAG(Z)=1
4200 IF RATIOFLG(Z)=1 THEN RATIOFLG(Z)=0:OLDSIG(Z)=1:NEWSIG(Z)=1
4210 PROP(Z) = KP(Z) * EROR(Z)/SET(Z)
4220 DERV(Z) = -KP(Z)*TAUD(Z) * DERIV(Z)
4230 IF (LASTPOS < 4) AND (FILENUM=0) THEN DERV(Z) = 0
4240 IF TEMP(Z)>=SET(Z)-SET(Z)/KP(Z) THEN TCOPUE=Z:GOSUB 3300
4250 INTE(Z) = KP(Z)/TAUI(Z) * INTEG(Z)
4260 IF (DERV(Z)>0) AND (PROP(Z)<0) AND (-DERV(Z)<PROP(Z)) THEN DERV(Z) = -
            PROP(Z)
4270 SIGNAL(Z) = (PROP(Z)+DERV(Z)+INTE(Z))*MAXSIG(Z)
4280 RETURN
4290 REM *****************************************
4300 REM *****************************************
4310 REM ***** This section prints system data to the terminal ****
4320 REM *****************************************
4330 CLS
4340 LOCATE 2,5
4350 PRINT "Elapsed time =":ELAPSE:"seconds ":"Marktime =":MARKTIME:"seconds"
4360 LOCATE 4,20
4370 PRINT "LOW MID(INF) TOP MIDETOP MIDTOPH INTLOWH"
4380 LOCATE 6,1
4390 PRINT "SETPOINT"
4400 LOCATE 6,19
4410 PRINT USING "####.####":SET(0),SET(1),SET(2)
4420 LOCATE 8,1
4430 PRINT "ACTUAL TEMP"
4440 LOCATE 8,19
4450 PRINT USING "####.####":TEMP(0),TEMP(1),TEMP(2),SAFETY(2),SAFETY(0),SAFETY(1)
4460 LOCATE 10,1
4470 PRINT "ERROR"
4480 LOCATE 10,19
4490 PRINT USING "###.###":EROR(0),EROR(1),EROR(2)
4500 LOCATE 12,1
4510 PRINT "SIGNAL"
4520 LOCATE 12,19
4530 PRINT USING "###.###":SIGNAL(0),SIGNAL(1),SIGNAL(2)
4540 LOCATE 14,1
4550 PRINT "PROPORTIONAL"
4560 LOCATE 14,19
4570 PRINT USING "###.###":PROP(0),PROP(1),PROP(2)
LOCATE 16,1
PRINT "DERIVATIVE"
LOCATE 16,19
PRINT USING "###.###": DERV(0),DERV(1),DERV(2)
LOCATE 18,1
PRINT "INTEGRAL"
LOCATE 18,19
PRINT USING "###.###": INTE(0),INTE(1),INTE(2)
LOCATE 20,1
PRINT "POWER (W)"
LOCATE 20,19
PRINT USING "##.##": AMP(0)*VOLT(0),AMP(1)*VOLT(1),AMP(2)*VOLT(2)

IF LOWER = 0 THEN GOTO 4760
LOCATE 22,1
PRINT "Percent Xtal"
LOCATE 23,1
PRINT "grown"
LOCATE 23,19
PRINT USING "###": TOTLEN/MAXLEN*100
RETURN

REM *****************************************************
REM *********** This routine turns on the power supplies ***********
REM *****************************************************
CALL DIGWRITE("lowps",1.)
CALL DIGWRITE("midps",1.)
CALL DIGWRITE("topps",1.)
RETURN

REM *********************************************************
REM *****************
REM **** This section ramps the temperature to set point ****
REM *****************
SWITCH(Z)=0
IF (DOWN(Z)=0 AND RATIOFLG(Z)=1) THEN RATIOFLG(Z)=0:OLDSIG(Z)=1:NEWSIG(Z)=1
IF (DOWN(Z)=1 AND RATIOFLG(Z)=0) THEN OLDSIG(Z)=SIGNAL(Z)
AVGDEL = (SET(Z) - AMBIENT(Z))/TIMETOT(Z)
LINEAR = AVGDEL*(ELAPSE - TIMESTART(Z)) + DELTAPOS*RAMPPROJ(Z) * SAMPRATE% * AMBIENT(Z)
DELTDES = (LINEAR-TEMP(Z))/RAMPPROJ(Z)*DELTAPOS
EXCONST(Z) = EXP(-DELTAPOS*SAMPRATE%/TAU(Z))
EXPFACT = 1-EXCONST(Z)
STEMP = DELTDES * 1/EXPFACT + TEMP(Z)
SIGNAL(Z) = (STEMP-SYSOFF(Z))/SYSR(Z)
IF (DOWN(Z)=1 AND RATIOFLG(Z)=0) THEN NEWSIG(Z)=SIGNAL(Z):
RATIOFLG(Z)=1
SIGNAL(Z) = ABS(OLDSIG(Z)/NEWSIG(Z)) * SIGNAL(Z)
RETURN

REM *********************************************************
REM **************
REM **** This routine assures that the system will respond to the
REM users
REM **************
REQUESTED TIME TO TEMPERATURE.
5050 REM  
5060 AMBIENT(Z) = TEMP(Z)  
5070 AVGDELT = (SET(Z)-TEMP(Z))/TIMETOT(Z)  
5080 IF AVGDELT > MAXRATE THEN 5130  
5090 MAXSST = AVGDELT*(1/(1-EXP(-SAMPRATE%/TAU(Z))))+SET(Z)  
5100 MAXSRAMP = (MAXSST-SYSOFF(Z))/SYSR(Z)  
5110 IF MAXSRAMP > MAXSIG(Z) THEN GOTO 5130  
5120 EFLAG=0 :RETURN  
5130 LOCATE 25,1  
5140 PRINT "ERROR  The system cannot reach set point in the requested time."  
5150 EFLAG=1:RETURN  
5160 REM  
5170 REM  
5180 REM *** This sections limits the maximum requested temperature. ***  
5190 REM  
5200 IF SET(Z) > MAXTEMP(Z) THEN GOTO 5220  
5210 EFLAG=0:RETURN  
5220 LOCATE 25,1  
5230 PRINT "ERROR  The requested setpoint is above the maximum safe temperature."  
5240 EFLAG=1:RETURN  
5250 REM  
5260 REM  
5270 REM **** Emergency termination procedure for excessive temperature  
5280 REM  
5290 GOSUB 6800  
5300 LOCATE 25,1  
5310 PRINT "Emergency shut off have exceeded the maximum allowed temperature!"  
5320 GOTO 6410  
5330 REM  
5340 REM  
5350 REM **** This section magnifies the plotter output  
5360 REM  
5370 PLOTMAG = 1 - PLOTMAG  
5380 PTFLAG=1  
5390 IF PLOTMAG = 0 THEN PFACTOR=1:POFFSET=0:PCENTER=0:RETURN  
5400 PFACTOR = 26 : POFFSET = SET(PLT) : PCENTER=5 : RETURN  
5410 REM  
5420 REM  
5430 REM ************ Termination procedure for excessive time  
5440 REM  
5450 GOSUB 6800  
5460 LOCATE 25,1  
5470 PRINT "Shut off have exceeded the maximum requested time."  
5480 GOTO 6410  
5490 REM  
5500 REM  
5510 REM ************ Termination procedure after maximum length is satisfied
5520 REM
5530 LOCATE 25,1
5540 PRINT "Stop pulling have grown the specified length of crystal."
5550 LOWSIG = 0
5560 LOWER = 2
5570 RETURN
5580 REM *****************************************************************************
5590 REM *********** This section changes the safety Trip points ***********
5600 REM *****************************************************************************
5610 CLS
5620 PRINT "This section changes the emergency shut off temperatures."
5630 PRINT "To escape type any number other than 0-3."
5640 INPUT "Which trip point should be changed, 0=bottom, 1=middle, 2=top, 3=safety":Z
5650 IF (Z>3) OR (Z<0) THEN RETURN
5660 INPUT "What is the maximum allowable temperature":M
5670 MAXTEMP(Z)=M
5680 RETURN
5690 REM *****************************************************************************
5700 REM *********** process control routine ****************************
5710 REM *****************************************************************************
5720 Z = PROCESS(PROC,1)
5730 TIMESTART(Z) = ELAPSE
5740 IF Z = 3 THEN GOTO 5910
5750 IF Z = 4 THEN GOTO 5980
5760 SET(Z) = PROCESS(PROC,2)
5770 IF SET(Z)=0 THEN SET(Z)=1
5780 TIMETOT(Z) = PROCESS(PROC,3)
5790 RAMPFLAG(Z)=0
5800 AMBIENT(Z)=TEMP(Z)
5810 IF (SET(Z)-AMBIENT(Z))/TIMETOT(Z)>MAXRATE THEN GOSUB 5130:GOTO 5830
5820 GOTO 5870
5830 GOSUB 6800
5840 LOCATE 25,1
5850 PRINT "ERROR The system cannot reach set point in the requested time."
5860 GOTO 6470
5870 IF TEMP(Z)>SET(Z) THEN DOWN(Z)=1:CALCSIG=(SET(Z)+SET(Z)/APP(Z)-
5880 SYSOFF(Z))/SYSR(Z) ELSE CALCSIG=(SET(Z)-SET(Z)/APP(Z)-
5890 SYSOFF(Z))/SYSR(Z):DOWN(Z)=0
5900 DERIV(Z)=0:INTEGR(Z)= CALCSIG/MAXSIG(Z)*TAUZ/KP(Z)
5910 PROP(Z)=0:DERIV(Z)=0:INTE(Z)=0
5920 GOTO 6010
5930 LOWRATE = PROCESS(PROC,2)
5940 MAXLEN = PROCESS(PROC,3)
5950 GEARRAT = PROCESS(PROC,4)
5960 TOTLEN=0
5970 LOWER = 1
5980 LOWSIG = -1 * LOWRATE* 2.778*.4153 *GEARRAT/50
5990 GOTO 6010
6000 MARKINT = PROCESS(PROC,2)
6010 Marklen = PROCESS(PROC,3)
6000 MARKSKIP = PROCESS(PROC, 4)
6010 PROC = PROC + 1 : GOTO 2220
6020 REM*****************************************************************************
6030 REM This routine views the process array ****************************
6040 REM*****************************************************************************
6050 CLS
6060 PRINT " 0"," 1"," 2"," 3"," 4"
6070 PN = 0
6080 WHILE PROCESS(PN, 0)<> 0
6090 PRINT PROCESS(PN, 0), PROCESS(PN, 1), PROCESS(PN, 2), PROCESS(PN, 3),
       PROCESS(PN, 4)
6100 PN = PN + 1
6110 WEND
6120 PFLAG = -1
6130 RETURN
6140 REM*****************************************************************************
6150 REM This routine allows modification of the process ******
6160 REM*****************************************************************************
6170 CLS
6180 PRINT " 0"," 1"," 2"," 3"," 4"
6190 PRINT "When","Zone","Temp/Low","TOT/LEN","Gearrat"
6200 INPUT "What process number (step) should be changed": PN
6210 IF PN > 50 THEN PRINT "Process number out of bounds": RETURN
6220 INPUT "What index value should be changed": I
6230 IF I > 4 THEN PRINT "Index value out of bounds": RETURN
6240 INPUT "What is the new value": VALUE
6250 PROCESS(PN, I) = VALUE
6260 RETURN
6270 REM*****************************************************************************
6280 REM This section changes the lowering rate periodically ******
6290 REM*****************************************************************************
6300 IF MARKNUM/MARKSKIP = INT(MARKNUM/MARKSKIP) THEN MARKNUM = MARKNUM + 1:
6310 GOTO 6390
6320 IF MARKON <= MARKLENG THEN GOTO 6350
6330 MARKNUM = MARKNUM + 1
6340 MARKON = 0
6350 MARKON = MARKON + 1
6360 IF MARKON > 1 THEN GOTO 6390
6370 TEMP = LOWSIG: LOWSIG = ALTSIG: ALTSIG = TEMP
6380 TEMP = LOWRATE: LOWRATE = ALTRATE: ALTRATE = TEMP
6390 RETURN
6400 REM*****************************************************************************
6410 REM This section terminates the data acquisition and program. ******
6420 REM*****************************************************************************
6430 EMERGOFF = 1 : GOSUB 1190
6440 IF ENDRUN < 3 THEN GOTO 6440
6450 NUMBR = FILENUM
6460 SKIP = CONVSKIP
6435 OUTNAME$=CONVNAME$
6436 CHAIN "convdta.bas",70
6440 STOP
6450 EMERGOF=0
6460 GOTO 1020
6470 REM ******************************************************************************
6480 REM **** This section checks for fuse failure ****************************
6490 REM ******************************************************************************
6500 FOR Z = 0 TO 2
6510 SIGERR(Z) = VOLT(Z)/MAXVOLT(Z) - SIGNAL(Z)/MAXSIG(Z)
6520 IF (SIGERR(Z) <= OLDSIGER(Z) OR VOLT(Z)< .1) THEN GOTO 6560
6530 BLOWFUSE(Z)=BLOWFUSE(Z)+1
6540 IF BLOWFUSE(Z) > 10 THEN GOTO 6600
6550 GOTO 6580
6560 BLOWFUSE(Z)=0
6570 OLDSIGER(Z)=.1
6580 NEXT Z
6590 RETURN
6600 GOSUB 6800
6610 CLS
6620 PRINT "Apparent fuse failure for fuse in zone ":Z;":"
6630 PRINT "Check board 5 on inside right of main power cabinet, especially grounds."
6640 PRINT "Another possibility is board 4 located directly behind the protective"n
6650 PRINT "rear cover (plastic) to the main power cabinet."
6660 PRINT "Causes for fuse failure include contacting of power leads with the case."
6670 PRINT "If fuses on board 4 have blown also check to make sure the polarity from"
6680 PRINT "the power supplies is correct."
6690 GOTO 6410
6700 REM ******************************************************************************
6710 REM ********** Shut down powersupplies at end of run ****************************
6720 REM ******************************************************************************
6730 FOR Z = 0 TO 2
6740 IF (SET(Z) < 100 AND SIGNAL(Z) < 0) THEN ENDRUN=ENDRUN+1
6750 NEXT Z
6760 IF ENDRUN < 3 THEN ENDRUN = 0: RETURN
6770 PRINT "Have successfully completed crystal growth program. GOOD LUCK!"
6780 GOSUB 6800
6790 GOTO 6410
6800 REM ******************************************************************************
6810 REM ********** Shut off relays to power supplies ****************************
6820 REM ******************************************************************************
6830 CALL DIGWRITE'("lowps",0.)
CALL DIGWRITE('"midps"',O.)
CALL DIGWRITE('"topps"',O.)
RETURN
REM
*****************************************************************************
REM ***** Help documentation
*****************************************************************************
CLS
PFLAG = -1
PRINT "Use lower case letters only."
PRINT "h = HELP", "d = DISPLAY DATA", "e = ERASE SCREEN"
PRINT "s = SET POINTS", "v = VIEW PROCESS ARRAY", "r = REDO PROCESS"
PRINT "p = PLOT ZONE", "m = MAGNIFY PLOT", "l = LOWER AMPULE"
PRINT "The following are not suggested." : PRINT
PRINT "c = CHANGE SYSTEM CONSTANTS", "t = CHANGE SAFETY SHUT OFF VALUES"
RETURN
REM
REM ***** Safety thermocouple shutoff
*****************************************************************************
FOR Z = 0 TO 2
IF SAFETY(Z) > MAXTEMP(3) THEN OVERTEMP(Z) = OVERTEMP(Z)+1
IF SAFETY(Z) < MAXTEMP(3) AND OVERTEMP(Z) > 0 THEN
OVERTEMP(Z) = OVERTEMP(Z)-1
NEXT Z
SHUTDOWN = 0
FOR Z = 0 TO 2
IF OVERTEMP(Z) > 10 THEN SHUTDOWN = SHUTDOWN+1
IF SHUTDOWN > 1 THEN GOTO 7120
NEXT Z
RETURN
GOSUB 6800
CLS
PRINT "A problem with thermocouples, two of the safeties sustained extreme temperature."
FOR Z = 0 TO 2
PRINT "Safety thermocouple #: "; Z; " Overtemperature factor ":"; OVERTEMP(Z)
NEXT
PRINT "Suggest evaluation of all thermocouples especially control TC for mid zone."
GOTO 6400
32. J.P. Hirth and J. Lothe, Theory of Dislocations, J. Wiley and Sons N.Y. 1982
33. E.L. Hall and J.B. VanderSande, Phil. Mag., 37 #1, (1978) 137
42. A.W. Vere, S. Cole, D.J. Williams, J. Electr. Mater., 12 #3 (1983), 551
43. R.W. Cahn, Adv. in Physics, 3, (1954), 202
46. This is believed to be an error since it gives a simple result of {1,1,2,2}. The authors probably meant {h,h,-2h,1}

- 233 -
55. M.J. Wargo, unpublished data
68. P. Becla, Personal communication
78. F.V. Wald and R.O. Bell, J. Crystal Growth, Vol. 30 (1975), 29
84. S. Sen and W.R. Wilcox, J. Crystal Growth, Vol. 28 (1975), 36
89. In reference to the mythological bird, and its own fiery rebirth
90. Courtesy of S. Motakef
91. Y.V. Rud and K.V. Sanin, Soviet Physics-Semiconductors, Vol. 5 #8 (1972), 1385
94. S. Motakef, To be Published
96. P. Griffin and S. Motakef, to be published Journal of Crystal Growth
97. P. Griffin, personal communication
102. As were conducted by D.H. Mathieson, personal communication
112. B. Fabes, MIT EROP project final report (1983)
126. R.E. Ogilvie, 3.081 class notes, Massachusetts Institute of Technology, 1981
132. Full diameter seeds courtesy of P. Becla and L. Colombo
133. Reduced diameter seeds courtesy of P. Becla and D. Hobgood
148. B.M. Kulwicki, Ph.D. Dissertation, University of Michigan, 1963
156. 155 Vol. 5
157. 155 Vol. 8
158. R.W. Balluffi, 33 Class notes, Massachusetts Institute of Technology, 1986

- 237 -