The Feasibility of Liquid Phase Electroepitaxial Growth of Cadmium Zinc Telluride

by

Neil Alexander Armour
B.A., University of California, Berkeley, 2002

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Abstract

Semiconductor crystals are of the foundation of the electronics industry. The widening field of applications for solid-state electronic devices has pushed the need for new, application tailored, semiconductor materials. Specifically, there is demand for production of compositional controlled ternary semiconductor materials.

The ternary material CdZnTe has been the subject of interest due to its attractive physical qualities. As a substrate, it is ideal for HgCdTe infrared detector applications. As a solid-state detector, CdZnTe is a very promising room-temperature gamma ray and hard x-ray detector. This kind of detector would see major application in the medical imaging field. Current commercial techniques have proved unsatisfactory in producing high quality CdZnTe material.

A new promising technique for producing bulk semiconductor crystals is liquid phase electroepitaxy, LPEE. As a solution growth technique, it avoids many of the problems associated with growing CdZnTe from the melt. This makes LPEE an attractive alternative to current growth techniques.

This study tested the feasibility of growing CdZnTe by LPEE. The interaction of CdZnTe with the LPEE system was thoroughly investigated. The result of the study was the successful initiation of LPEE growth. LPEE is a promising technique for producing high quality material. Some difficulties remain with the growth system that were beyond the scope of this study, such as the contact zone. Further study is necessary to mature this technique.

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Acknowledgments

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Section 1

Introduction

1.1 Motivation

Cadmium zinc telluride, CdZnTe, is a very difficult material to produce. There is no mature commercial growth technique for producing high quality material [1, 2, 3, 4, 5, 6, 7]. Current techniques are expensive and do not have high yields. This has led to high material cost, which in turn has limited the use of devices based on CdZnTe [8, 9, 10, 11, 12].

Devices based on CdZnTe are attractive in a number of applications. CdZnTe is used as the substrate for high quality mercury cadmium telluride, HgCdTe, infrared detectors [13, 14, 15]. Other substrates have been used with HgCdTe, but CdZnTe allows the substrate to be ideally lattice matched to the device layer. A better lattice match between the substrate and device layer leads to a higher quality device. At the other end of the spectrum, CdZnTe is used as a material for x-ray and gamma ray detectors [16, 17, 18, 19, 20]. Detectors based on CdZnTe can operate at much higher temperatures than current high-energy radiation detectors. This removes the requirement of a cryogenic cooling apparatus for the detector. Germanium based detectors, for example, require an operating environment temperature of only a few Kelvin. This significantly reduces costs associated with systems based around a solid-state detector. X-ray and gamma ray detectors such as this have a large market in the medical imaging sector [21, 22, 23].

CdZnTe is commercially grown by two main methods, Czochralski and Bridgman [24, 25, 26, 27, 28]. Both techniques require the use of high pressure or a combination of pressure and encapsulant. These requirements raise the cost of the produced material. In addition, melt growth techniques, such as Czochralski and Bridgman, are not well suited to producing uniform ternary material. An emerging growth technique is the traveling heater method, THM. This technique can produce quality ternary material, but the yield of material is reduced. THM is not as of yet a mainstream commercial growth technique.

Liquid phase electroepitaxy, LPEE, is a growth technique that can produce superior quality ternary material [29, 30, 31, 32]. Crystals grown by LPEE will have significantly reduced crystal defects and will have uniform composition throughout. There are significant disadvantages with LPEE growth as well. Growth is slow and the volume of material produced is low. Despite this, LPEE remains an attractive growth technique due to the promise of high quality reproducible material.

It has been undertaken in this study to modify an existing, highly successful, gallium indium arsenide, GaInAs, LPEE growth system for use with CdZnTe. This project has involved a redesign of the growth crucible. Material interactions have proved significant obstacles.

1.2 Approach

This study's purpose is to prove experimentally the feasibility of LPEE growth of CdZnTe. At the University of Victoria, GaInAs crystals have been successfully grown by LPEE. This apparatus was used as the starting point for this study.

Initial trials of CdZnTe were run on the GaInAs system with no modifications. These runs were used to identify problems. Once problems were identified, the offending part of the system was isolated. Systematic modifications were made until a satistfactory solution was reached. The system was then retested as a whole and remaining problems systematically eliminated.

1.3 Outline

This thesis will begin with a background discussion of semiconductor material and crystal growth. The reasons for pursuing LPEE as a growth technique will be examined. The properties of CdZnTe will be also be discussed.

The following section will discuss the experimental procedure. This section indicates the various trials conducted, the problems encountered and the solutions reached. Finally, the results of the growth trials are examined.

Section 2

Background

This section will introduce the background information on topics closely related to the work being presented. The topics described here will be briefly presented.

2.1 Crystallography

The properties of semiconductors are tied to their physical structure. The majority of semiconductors are solid crystalline materials. As such, basic knowledge of the principles of crystal structure is needed for full appreciation of semiconductor behavior.

2.1.1 Crystal Lattice

In a gas, liquid, or amorphous solid all the directions are statistically equivalent. This kind of material will have homogeneous properties over all directions in a volume. This is not necessarily true when considering crystal structures. A crystal structure is a pattern that repeats in space. The spacing between constituent atoms is repeated in a given direction, but there is not necessarily the same spacing in all directions. Thus, there is a defined orientation to the solid. This is important when considering physical properties. Physical properties can change depending on the direction within the solid that is considered. This behaviour is not seen in directionally equivalent materials. An example of this is evident when considering crystal growth. The growth rate of a crystal is often dependant on which direction the growth is proceeding along [33]. Crystal structure is generally unique to a material. It is determined by the nature of the bonding between the constituent atoms.

The most basic structure in crystals is the unit cell, which repeats to build the lattice. The lattice is a regular repeating pattern of points in space. A lattice translation is defined as a vector that moves from one point in the lattice to another. Further, these translations are minimized such that there are three unique vectors, which translate to the three closest unique lattice points. The lattice axes are the directions defined by the three minimized lattice translations.

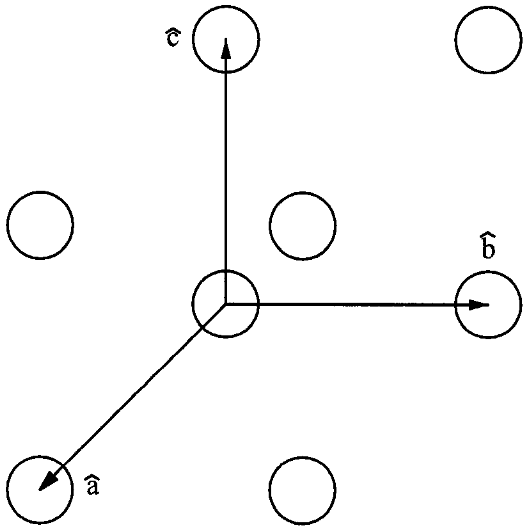


Figure 2.1: The above is a sample cubic crystal lattice. The lattice sites are indicated by the circles. The lattice translations are indicated by the arrows.

The length, or norm, of a lattice translation is known as the lattice parameter. The lattice parameter of a crystal is the physical distance between lattice points on a given crystal axis.

All lattice points are equivalent due to the nature of the repeating pattern. The origin can be defined as any lattice point.

The lattice translations form a basis and can be written as the vectors $\hat{a}$, $\hat{b}$, and $\hat{c}$. This is indicated in Figure 2.1. Any lattice point can then be defined, in relation to an origin, by the linear combination $u\hat{a} + v\hat{b} + w\hat{c}$. In a given lattice, each lattice point is uniquely defined by the set of numbers uvw. The linear combination also defines a direction. This direction is denoted $[uvw]$. This direction is independent of the choice of origin, due to the equivalence of all lattice points. In this notation scheme, negative numbers are indicated by a bar over the effected number [34].

2.1.2 Crystal Planes

The crystal planes, like the direction $[uvw]$, are independent of origin choice. Three points are required to define a plane. The points where the plane intersects the lattice axes are taken as these points. The intersection points will be represented by the numbers m, n, p. These three numbers completely define the plane in question. The general equation for a plane is the following,

$$\frac{X}{x} + \frac{Y}{y} + \frac{Z}{z} = C \tag{2.1}$$

X, Y, and Z are points in the plane. x, y, and z are the intersections with the axis. The constant C accounts for parallel planes.

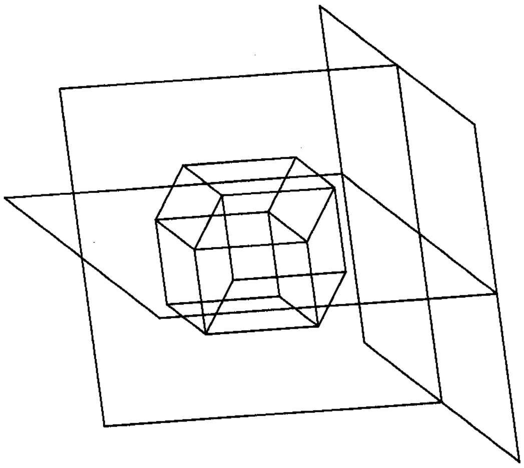


Figure 2.2: This diagram shows a trigonal crystal lattice, typical of common quartz. Three of its crystal planes are indicated by the superimposed rectangles. Quartz crystals take on the trigonal shape at a macroscopic scale. This is typical of lattice structure affecting crystal morphology.

The simplest case of planes passing through the origin is considered as the basic plane. This means that C is set at zero. For simplicity, the planes are identified by the reciprocals of the intercepts. Therefore,

$$\begin{aligned} h &= \frac{1}{m} \\ k &= \frac{1}{n} \\ l &= \frac{1}{p} \end{aligned}$$

The numbers h, k, and l when expressed in the form (hkl) are known as Miller indices. This is the most common way of specifying crystal planes. h, k, and l are normally written as integers as this usually only involves a change of origin, which does not effect the definition [35]. Figure 2.2 illustrates three crystal planes present in a trigonal lattice.

Crystal planes are to be carefully considered in semiconductor applications. The lattice parameter can vary between the plane that is chosen. This needs consideration when matching device layers to substrates. In addition, in a zinc-blende lattice like CdZnTe there are two (111) planes. One plane has all lattice sites filled with Te. The other has sites filled with Cd and Zn. This makes the properties of these two planes distinct [36, 37].

2.1.3 Crystal Basis

In general, crystal structures are not built as simply as one atom at each lattice point. In the previous discussion, we noticed that every lattice point is equivalent. For this to hold, whatever is inserted at a lattice point must be inserted in the exact same way at every other lattice point. This means multiple objects can be inserted at the same lattice point provided that they are inserted in the exact same orientation. An example of this could be inserting a molecule at every lattice point, with the molecules orientation kept the same from point to point. The arrangement of individual atoms within the lattice is called the basis. The basis is written as fractions of the lattice translations. Each object, which is part of the collection being inserted, has its own basis coordinate.

The basis causes the formation of congruent lattices. This is best illustrated with an example, see Figure 2.3. Consider, a cubic lattice of element A with element B inserted with a basis of x,y,z. This lattice could also be seen as two cubic lattices, one of element A and one of element B, offset from one another by x,y,z. Element B's lattice is a congruent lattice [34].

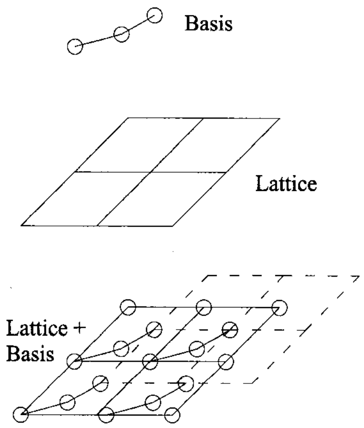


Figure 2.3: A crystal basis and its congruent lattices. Only one of the two congruent lattices is indicated. The lattice indicated with the solid lines is a cubic lattice of element A. The congruent lattice indicated by the dashed lines is formed by element B.

2.1.4 Symmetry Operations and Bravais Lattices

The repetitive nature of a crystal lattice leads to symmetry within the lattice. Types of symmetry include inversion points, rotation axes and mirror planes. New lattice sites can be added to a lattice provided they do not disrupt its symmetry. This would seem to further expand the number of lattice types available. This is not the case, as most of the time the resulting lattice can be simplified to a more basic configuration. To fill a three dimension volume with a regular repeating pattern, there are only fourteen lattice types available. These are known as the Bravais lattices and are indicated in Figure 2.4. All solid crystalline materials possess one of these lattices [34].

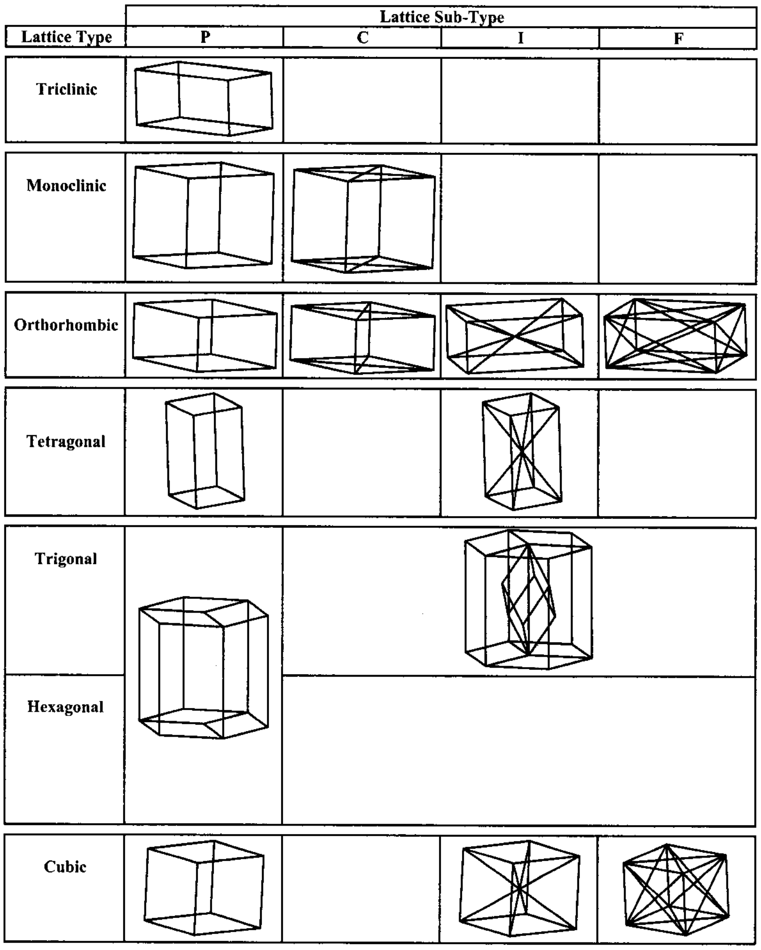


Figure 2.4: The 14 Bravais Lattices. The sub-type P refers to the primitive, or basic, lattice. The other subtypes are generated by inserting new lattice sites at symmetry locations,

2.1.5 Defects

Lattice defects profoundly effect the electrical properties of the semiconductor material. The various types of defects will be discussed in the following sections.

2.1.5.1 Point Defects

Point defects refer to errors in the lattice at a single point. Impurity atoms present in the lattice are an example of a point defect. Impurities may or may not be at a lattice point. Impurities at a lattice point are a substitutional defect. An impurity or an atom from the material in a position in between lattice points is an interstitial defect. In addition to these types of defects, there are vacancy defects. A vacancy is simply an unoccupied lattice site. If an interstitial and vacancy occur together, the situation is referred to as a Frenkel pair. These point defects are indicated in Figure 2.5. The defects serve to alter the lattice parameter in the area around the defect, introducing strain. In addition, impurities can change the material's properties. Semiconductors are often doped with impurities atoms to alter their electric properties [38, 39].

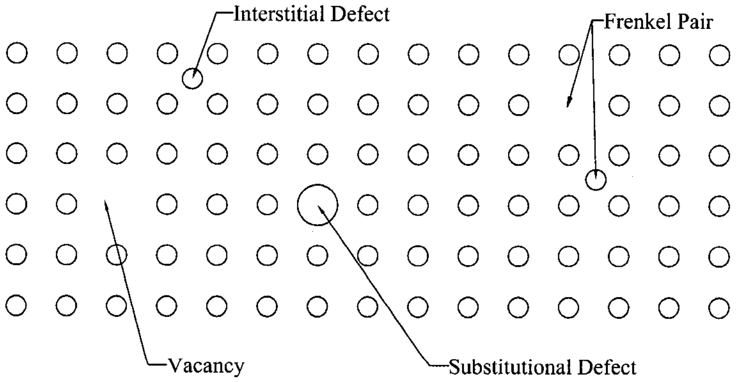


Figure 2.5: The four types of point defects are indicated above.

2.1.5.2 Dislocations

Crystalline materials have a lower critical shear stress than theory would predict for a perfect lattice. This is due to line defects known as dislocations. Dislocations allow slip to easily take place within the lattice. A dislocation lowers the number of bonds that have to be broken to allow slip to occur.

Dislocations are broken into two categories, edge dislocations and screw dislocations. An edge dislocation can be thought of as an extra lattice plane. A four by four two dimensional array of lattice points will have an edge dislocation if we squeeze an extra half plane, two points, into the middle of the lattice from a surface. The new plane sustains the lattice on either side, but the end of the new plane does not match up with the lattice below. At the middle of the original four by four array, there are now three planes trying to link with two. This can be extended to three dimensions by stacking the described two dimension lattice. In this type of dislocation, slip takes place normal to the face of the inserted plane. Returning to the two-dimensional example, as shear stress is applied the dislocation moves in the direction of slip. The dangling ends of the extra plane mean fewer bonds have to be broken for slip to take place. This is illustrated in Figure 2.6

Screw dislocations are the other type of dislocation. A screw dislocation marks the boundary between slipped and unslipped regions of the crystal. In the transitional region between the slipped and unslipped volumes, slip more easily takes place. This type of dislocation moves into the unslipped region with applied shear stress. The direction in which the dislocation moves is perpendicular to the slip direction and is illustrated in Figure 2.7

Most dislocations found in crystals are not purely edge or screw type. Instead, combinations of the two types are the most common dislocations [40].

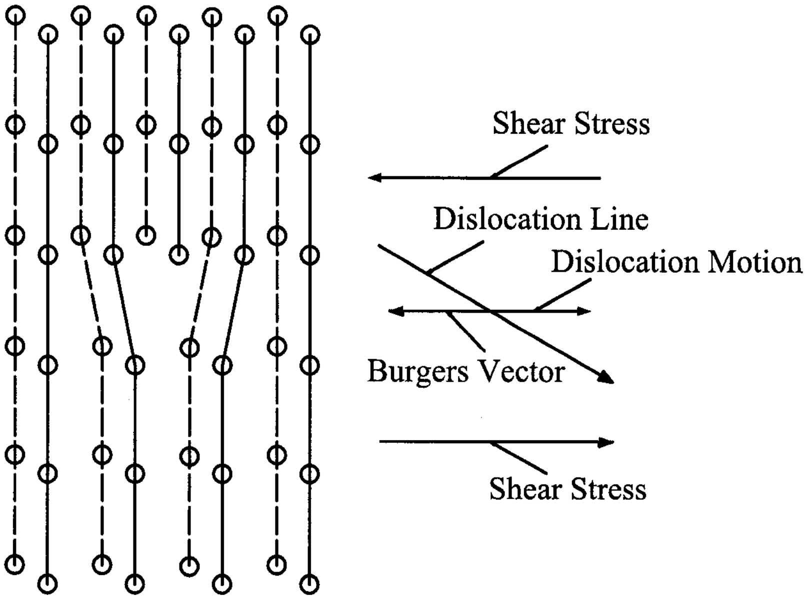


Figure 2.6: A line dislocation and its relevant vectors are shown.

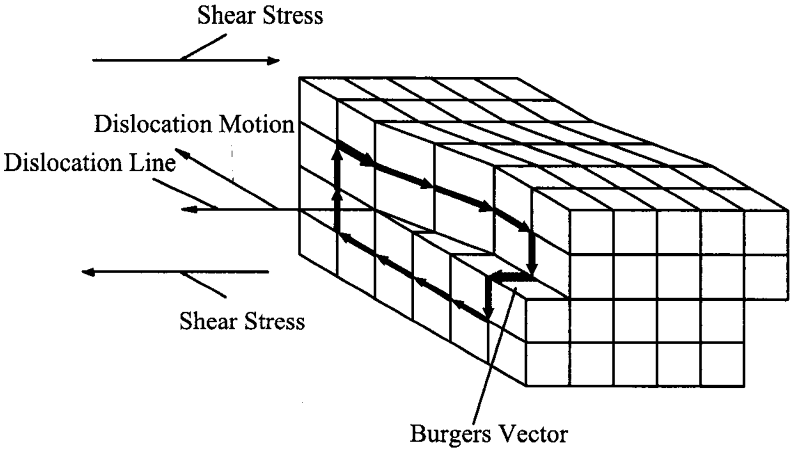


Figure 2.7: A screw dislocation and its relevant vectors are shown.

2.1.5.3 Stacking Faults

Stacking faults occur when the stacking order for the crystal planes become disordered. For example, if the stacking order is ABCABC, a stacking fault would be ACBABC. The capital letters each represent a distinct lattice plane. Stacking faults lead to increased internal strain and compromised electrical properties.

A related phenomenon is twinning. Twinning occurs when the crystal mirrors itself around some given axis. A twinning fault would appear as ABCABCBACBA [40].

2.1.5.4 Grain Boundaries

In polycrystalline material, grain boundaries are where two crystal orientations meet. At these boundaries all the crystal defects are common. The intersecting lattice orientations cause high strain, which helps with the formation of the other defects. Grain boundaries present in a melt grown CdZnTe ingot are shown in Figure 2.8.

Figure 2.8: Section of CdZnTe showing some grain boundaries. This crystal is from the Vertical Gradient Freeze experiments conducted at the University of Victoria.

2.2 Semiconductor Electronic Behavior

Semiconductor materials exhibit conductivity between that of insulators and conductors. Rough divisions by conductivity can be made as follows. Conductors are generally considered materials having conductivities at or above $10^4 Scm^{-1}$. Insulators are generally defined as materials having conductivities below $10^{-8} Scm^{-1}$. The gap between these two regimes is where the semiconductors lie. A pure, intrinsic, semiconductor is neither a good conductor nor a good insulator [40].

2.2.1 Energy Band Structure

A band structure of energy levels arises from the crystalline structure of the semiconductor. Specifically, the periodic potential created by the regular spacing of atoms, as found in a lattice. The periodic potential constrains the energy levels into distinct bands of energy levels. The actual energy levels are close together in energy, but the bands can be widely spaced. When the electrons in an atom are each at their lowest energy level this is said to be the ground state. The highest band in energy with electrons in it is the valence band. The band above this is referred to as the conduction band. The spacing between the valence and conduction bands determines the conductivity of the material. Good conductors will have the valence and conduction bands overlapping. Insulators will have the bands widely spaced. Semiconductors are, again, somewhere in between the two extremes. For electrons to conduct they need to gain enough energy to jump from the valence band to the conduction band. This is easier for metals, smaller gap and less energy required, and harder for insulators, larger gap and more energy required. The gap between the valence band and conduction band is called the band gap. This is an important quantity for classifying semiconductors. A typical band structure is illustrated in Figure 2.9.

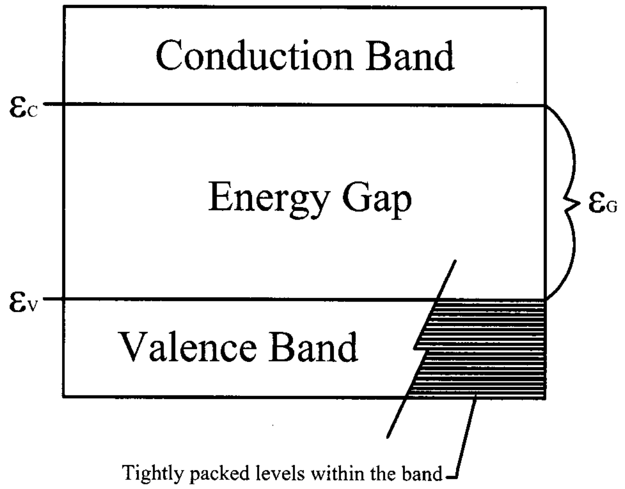


Figure 2.9: Diagram of the energy band structure indicating the fine structure within a band.

The mechanisms for exciting electrons across the band gap range from thermal effects, photon interactions, applied fields and many others. When designing a solid-state detector, such as a charge-coupled device, the semiconductor material chosen has a band gap such that the energy of light being observed will create numerous conduction electrons. This charge is then recorded and the intensity of the light deduced [41].

2.2.2 Conduction in Semiconductors

Intrinsic, un-doped, semiconductor materials have low conductivities. They usually have a complete valence band of electrons. When a conduction electron is produced in an intrinsic semiconductor there are actually two charge carriers produced. There is the electron in the conduction band and there is also the hole in the valence band. The hole in the valence band can be thought of as a positive electric charge carrier. When holes conduct they exhibit similar behavior as electrons. This is because both conduction methods

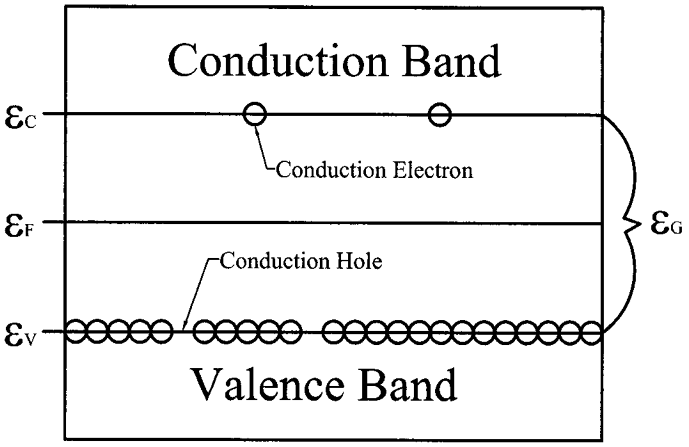


Figure 2.10: The diagram above shows an intrinsic semiconductor where two electron–hole generation events have occurred. Electrons moving in the valence band can transport the hole, effectively moving positive charge.

involve electron movement. In the holes case, it is electrons moving between valence bands. This is indicated in Figure 2.10. ϵ_C is the energy associated with the lower edge of the conduction band. ϵ_V is the energy of the top edge of the valence band. ϵ_G is the energy difference or band gap. A pair production event must transfer energy of at least ϵ_G to be successful. ϵ_F is the Fermi energy. This is an indication of whether the semiconductor forms holes or conduction electrons. When it is in the center of the band gap the semiconductor is an intrinsic semiconductor and will form only hole–electron pairs.

It is often desirable to increase the conductivity of a semiconductor. This is accomplished by introducing excess charge carriers into the material. Doping the intrinsic semiconductor with impurities is the method employed to add excess carriers. If the impurity atoms contain more electrons in its valence shell than the semiconductor atoms they are replacing, then excess electrons have been added. This moves the Fermi energy up towards the conduction band. This type of doping makes the semiconductor n type. If the impurity atoms have less electrons, the semiconductor has extra holes and is said to be p type [40].

2.2.3 Semiconductor Materials

2.2.3.1 Elemental Materials

Two of the most common semiconductors are silicon and germanium. These elements in their crystalline form are good semiconductor materials. The majority of electronic devices are based around silicon semiconductor technology. Silicon and germanium are the common elemental semiconductors because they possess favorable band structure. Both elements are from the IV column of the periodic table. Other elements in this column also exhibit semiconductor characteristics. One such example is carbon [40].

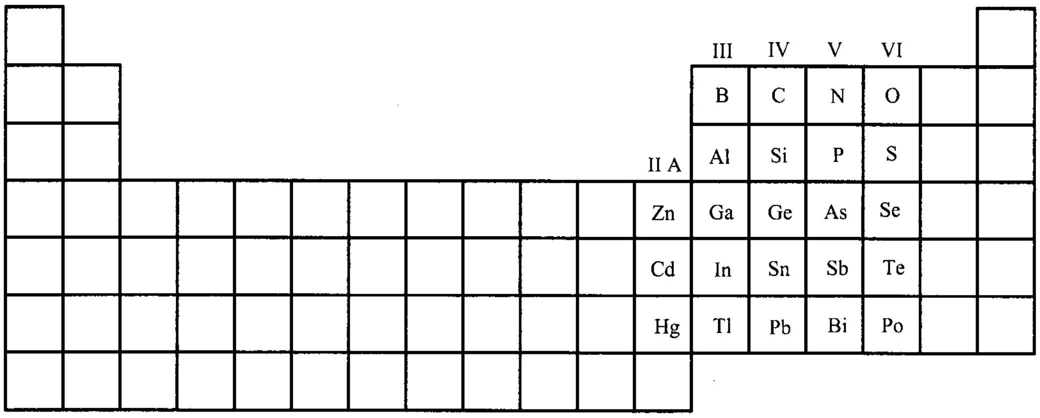


Figure 2.11: The common semiconductor columns on the periodic table.

2.2.3.2 Binary Materials

Compounds as well as elements exhibit semiconductor properties. Binary semiconductors are two element compounds. Semiconductor compounds, like elemental semiconductors, possess favorable band structure. They are commonly formed by elements from the III column of the periodic table and the V column. The columns on the periodic table that the semiconductor elements come from are indicated in Figure 2.11. Such materials are referred to as Type III-V. Examples of these materials include GaAs, InAs, GaSb and InSb. In addition to Type III-V binaries there are also Type II-VI binaries. These are compounds formed from elements of columns II A and VI. Examples of these include ZnTe, CdTe, CdSe, ZnSe. Another common binary semiconductor is SiGe, which is a Type IV-IV material. The Type II-VI and Type III-V materials are most often compounds with strong chemical bonds between the two elements. The elements are often in stoichiometric ratios. For SiGe, the mixture is a solid solution over the compositional range. Therefore, the properties of the semiconductor will change depending on the composition of the material. For most binaries this is not the case [42].

2.2.3.3 Ternary Materials

Ternary semiconductor materials are similar to the SiGe binary discussed earlier. Ternary materials can be considered a mixture of two binary semiconductors. These form a solid solution over a compositional range. The composition will determine the semiconductor properties. GaInAs is a Type III-V ternary and can be considered a mixture of GaAs and InAs. Similarly, CdZnTe is a Type II-VI ternary and can be considered a mixture of CdTe and ZnTe [19].

2.2.3.4 Quaternary Materials

Quaternary materials are mixtures with even more elements and are extensions of the ternary idea. They allow tuning of semiconductor properties to a very specific application. One example of a quaternary is AlGaAsP. This can be considered a mixture of AlGaAs and AlGaP. Both of these ternaries are then mixtures of binaries. The extra elements in these materials allow for ideal tuning of the semiconductor's electrical properties [19].

2.2.3.5 Band Gap Engineering

As has been discussed, using compounds allows the semiconductor's properties to be tuned to an application. One of the properties that is being tuned is the band gap. This property defines the semiconductor's conduction characteristics. Returning to the example of CCD photon detectors, the CCD material's band gap can be changed so its highest response is at the photon energy that is being measured. This allows the production of very high sensitivity detection devices [38].

2.2.3.6 Lattice Matching

Many semiconductor devices are grown as thin layers on thick substrate materials. An example is a HgCdTe infrared detector. The HgCdTe layer is grown on a CdZnTe substrate. Growing a thick HgCdTe layer is impractical due to the material's properties. Similar situations exist for many other materials. The thin layer and substrate should have similar lattice parameters. Recall that the lattice parameter is the distance between lattice sites. If the lattice parameter is not similar, strain will be present across the device layer–substrate interface. Strain will lead to dislocations and other defects that adversely affect the device's electronic properties [38].

One solution is to use compositionally graded device layers to minimize strain. In this method, the first layer applied to the substrate is closely matched to the substrate lattice parameter. Later layers gradually deviate from the first composition until the required device composition is reached. This method is involved and only minimizes the strain problems. The ideal solution is to use a substrate matched to the device layer. Using compound materials allows for lattice matching. Varying the composition of the compounds affects the lattice parameter of the crystal. Using compounds to generate ideally matched substrates results in production of high quality device layers [29].

2.3 Crystal Growth

Crystal growth is concerned with the production of crystalline materials. In semiconductor applications single crystal material is desired. This means the entire volume is free from grain boundaries. Low defect density is also of prime concern.

2.3.1 Bulk Growth

The topic of this thesis is concerned with bulk crystal growth. Bulk growth can be defined as growth on the millimeter scale. Device layer techniques are generally below this on the micrometer and nanometer scales. Substrates for devices are produced from bulk crystals. The following techniques can all be applied to bulk growth.

2.3.2 Solid Phase Techniques

Solid phase techniques rely on solid-state diffusion for growth. As such, growth rates are very slow. Slow growth rate makes yields low and generally these techniques are uneconomical. Solid phase techniques are avoided unless there is no other viable option [33].

2.3.3 Vapor Phase Techniques

Growth from the vapor phase is another group of slow growth rate techniques. Growth from the vapor phase is often used for device layers. The techniques produce material of excellent composition and low defect density.

However, the low growth rate is a large handicap for bulk growth. Vapor phase techniques include Molecular Beam Epitaxy, Physical Vapor Transport and Metal Organic Chemical Vapor Deposition. Again, for growth rate concerns vapor techniques are avoided [43, 44, 45].

2.3.4 Melt Growth Techniques

Melt growth techniques are the dominant growth techniques for commercial applications. They offer high growth rates and yields. Melt growth involves raising the material's temperature to above its melting point and freezing out a crystal. The major drawback with melt growth becomes evident when growing compound materials. There is often a large separation between the liquidus and solidus lines for compound materials. Therefore, as the melt crosses the liquidus line it is in equilibrium with a solid of different composition. As solidification proceeds the composition of the melt will change. The result is compositional variations throughout the grown material. The following is a brief description of the important melt growth techniques.

2.3.4.1 Czochralski Method

The Czochralski method is a pulling technique. A seed crystal is slowly pulled out of a reservoir of melt. As the seed moves from the reservoir it cools, which solidifies the melt pulled with it. In this way, large crystals can be grown. A typical Czochralski apparatus is shown in Figure 2.12. In fact, this method is the predominant crystal growth technique for commercial production. For silicon, single crystals of 6 inch diameter and 4 foot lengths and larger can be grown. High temperatures are required for this technique resulting in thermal stresses in the grown material. Evaporation of material can also be a concern. In these cases, the melt reservoir is often encapsulated to prevent losses. A common melt encapsulant is boron oxide [28].

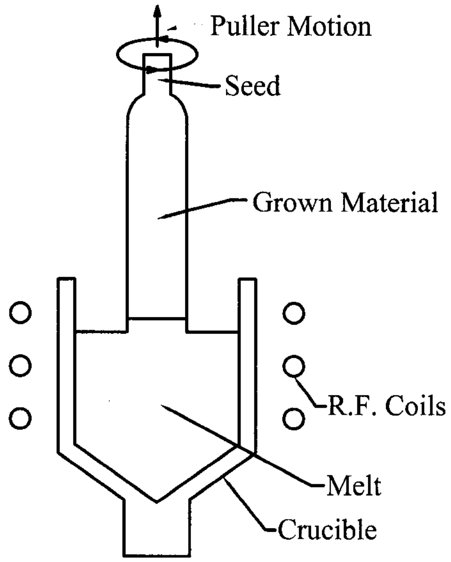


Figure 2.12: Schematic of a typical Czochralski Apparatus.

2.3.4.2 Bridgman Method

The Bridgman method is another widely used growth technique. In this method the melt is moved through a temperature gradient. The melt freezes as it passes its melting point on the temperature gradient. The Vertical Gradient Freeze technique is a variant of Bridgman [24, 46]. In this technique the crucible is held stationary and the temperature profile is moved. These methods and the Czochralski method suffer from similar problems like thermal stress and compositional variations [21, 25, 26, 27].

2.3.5 Solution Techniques

The solution growth techniques involve a solvent and solute setup. The solvent can either be one component of the compound semiconductor being grown or a separate material. The solution is heated to its saturation temperature rather than the compound melting point. Growth is usually initiated on seed material. Growth proceeds by supersaturating the solution in the region where the solution contacts the seed. Super–saturation is induced in a number of ways depending on the technique.

2.3.5.1 Traveling Heater Method

The traveling heater method involves passing a solvent zone through feed material. A steep temperature profile isolates the molten solvent zone. The crucible is moved through the temperature profile. This initiates growth onto the seed as the temperature of the solution decreases. At the same time, the feed material is being dissolved keeping the solution saturated. Like most solution growth techniques, THM suffers from low growth rates and yields [47, 48, 49, 50, 51, 52].

2.3.5.2 Liquid Phase Epitaxy

Liquid phase epitaxy is another common solution growth technique. In this technique, a saturated solution is introduced onto a seed crystal and the temperature is dropped. Layers are precipitated onto the seed. The use of source material will allow this process to cycle and can result in the growth of thick layers. Although, typically liquid phase epitaxy is used for thin layer preparation [3, 9, 53]. A typical LPE apparatus is illustrated in Figure 2.13.

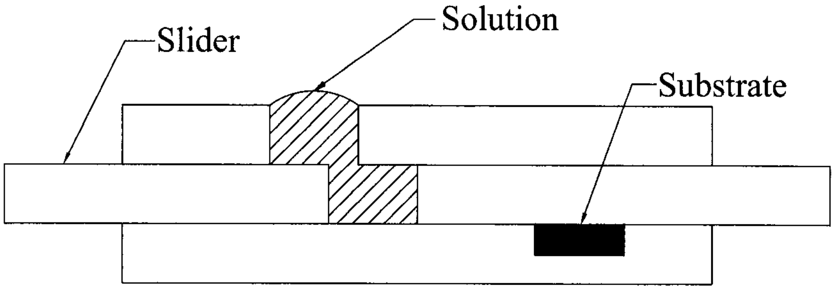


Figure 2.13: Schematic of a typical LPE crucible.

2.4 Liquid Phase Electroepitaxy

Liquid phase electroepitaxy, LPEE, is a variant of the liquid phase epitaxy technique that has showed promise as a bulk growth technique. It was chosen as the growth technique in this study due to the problems involved with producing CdZnTe by other techniques, such as thermal defects and zinc segregation.

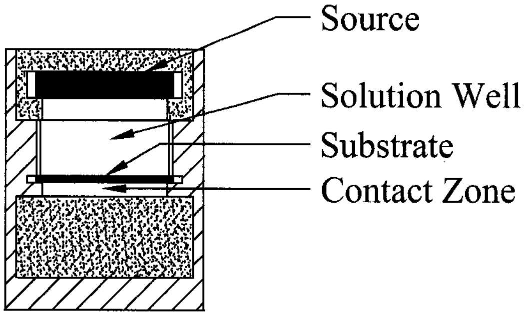


Figure 2.14: Schematic of a LPEE Growth Cell.

2.4.1 Growth Mechanisms

The growth in LPEE is driven by thermo–electric effects. The growth cell consists of a seed and source separated by a saturated solution. A schematic of the growth cell is shown in Figure 2.14. The solution composition depends upon the desired material composition and the growth temperature. The seed is a single crystal, which is either the same as the material being grown or another closely matched material. The source is usually a polycrystal of composition identical to the material being grown. The back of the source and seed are connected to isolated electrodes, and current is passed across the solution.

2.4.1.1 Peltier Heating/Cooling

One mechanism that aids growth is the Peltier effect. This is a heating or cooling caused by current passing across an interface between materials of differing conductivity. The effect can be thought of as a compression or expansion of the electron gas as it transitions between materials. The electron gas does work against the potential barrier that equalizes the chemical potential across the interface. In the case of the seed-solution interface, cooling takes place as the electron gas expands from the high conductivity solution to the low conductivity seed [54]. The reverse takes place at the source as the current goes from a low conductivity to high conductivity material. The cooling at the seed interface helps to super-saturate the solution along the interface and initiates growth. The heating at the source interface causes the solution to be slightly dilute and therefore helps with source dissolution. Dissolution of the source keeps the solution saturated and allows growth to continue to significant thicknesses [55, 56].

2.4.1.2 Electromigration

The major contribution to the growth rate comes from electromigration. Electromigration results from momentum exchange between current charge carriers, electrons, and the atoms or molecules in the solution. As the charge carriers cross the solution they transport solute in the same direction. This process is shown in Figure 2.15. This sets up a concentration gradient across the solution between the source and substrate. The higher concentration of solute at the seed interface leads to super-saturation and the initiation of growth. Convection will suppresses electromigration by continually remixing the solution. This inhibits the formation of a concentration gradient [55, 57].

The relative contributions of electromigration and Peltier cooling to the overall growth rate are determined by the growth cell geometry. Specifically, if the current is allowed to bypass the source, the growth mechanism will primarily be electromigration. If the current must pass through the source, Peltier cooling will play a more dominant role. The difference arises from the contribution of Joule heating to the temperature profile. The choice between these two geometries has a profound effect on growth interface shape. When electromigration is dominant, the interface shape is much flatter resulting in a flatter composition profile along the radial direction through the grown material [58, 59, 60, 61].

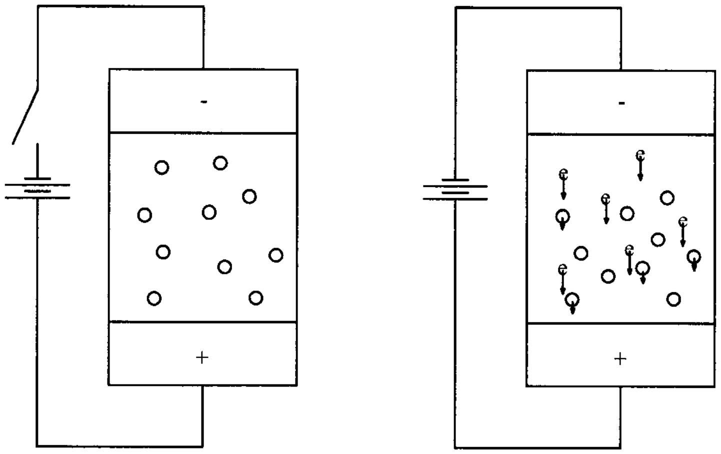


Figure 2.15: The above diagram indicates the transport of solute by electromigration. The solute is indicated by the circles and the solvent is the backdrop. When the DC supply is connected the flowing electrons, indicated with an "e", transfer momentum to the solution. The momentum transferred to the solute transports it to the substrate interface.

2.4.1.3 Joule Heating

Joule heating is a thermoelectric effect that detrimentally affects LPEE. Joule heating refers to heat generation arising from passing current through a resistive material. The amount of heat is proportional to the material resistance. For a semiconductor with relatively high resistance, the amount of heat evolved is quite large. This can start as a few degrees Celsius and will increase with the thickness of the grown layer. The amount of heat evolved increases with a longer current path through the material. As material grows on the substrate, the heat being evolved from Joule heating is increasing. The increased heat evolution will start to offset the contribution of Peltier cooling to growth and dilute the solution causing electromigration growth to slow. In addition, current passing through the source will cause it to heat as well. This will contribute to convection in the system and suppress electromigration [55, 56].

2.4.2 Preparation

There are various choices to be made in the preparation of the LPEE growth cell. The most important involve the solution and contact zone. The contact zone refers to the electrical contact between the seed and its electrode.

2.4.2.1 Solution

The solution composition determines the growth temperature for the experiment. The growth temperature can be adjusted by changing the relative amounts of solvent and solute in the solution according to the material's phase diagram. In the case of CdZnTe, increasing the amount of solvent Te lowers the material melting temperature. This allows growth to take place at temperatures lower than the melting temperature. This alleviates problems normally associated with melt growth such as segregation, thermal stress and vapor pressure issues. In the case of CdZnTe, LPEE experiments took place at $800°C$ while melt growth techniques require temperatures of over $1050°C$ [62, 63].

The solution material must be saturated at the growth temperature. This requires specific attention to the material's phase diagram. An unsaturated solution will cause melt back of the substrate and source until the solution saturates and growth can proceed. This situation is to be avoided as it will produce unpredictable results. To prepare the growth cell, the solution is melted and allowed to come to saturated equilibrium away from the substrate. A secondary source is sometimes used in the solution preparation to ensure saturation. Only once growth temperature is reached and time is allowed for the solution to reach a saturated state is it introduced into the growth cell between the source and substrate.

2.4.2.2 Contact Zone

The contact zone material is another major consideration. It is imperative in LPEE that the electrical contact between the seed and electrode be as perfect as possible. This is a requirement for even growth across the interface. To achieve this there are a number of options available. For GaAs, a liquid zone was used very successfully. Also, in similar experiments a Ga wetted inert metal foil was used between the seed and electrode [31, 32, 55, 56].

The considerations when choosing a contact zone start with material properties. In addition to being a good conductor, the contact zone should not interact with the seed. Also, thought needs to be given to separating crystal and contact zone after the experiment. Preparation of the contact zone can also be problematic. The electrical contact between the seed and electrode must be as uniform as possible. With a liquid contact the volume between the seed and electrode must be completely filled. This can be difficult to achieve [29].

The contact zone proved to be a difficult matter with LPEE growth of CdZnTe and all manners of contact zones were tested.

2.4.3 Disadvantages

Liquid phase electroepitaxy has some major disadvantages. The most important of which is growth thickness. Due to the mechanisms involved, growth is limited to approximately $3 - 5mm$ [32]. This is very little compared with melt growth techniques. The low growth makes LPEE a much more expensive way to produce material. Growth thickness increases have been achieved using static magnetic fields to suppress convection. In these cases, material of up to $10mm$ thick has been achieved [30, 64, 65]. This helps tremendously with the growth thickness problem, but $10mm$ is still a much lower yield than melt growth techniques.

The grown crystal thickness will have a critical thickness due to Joule heating. Joule heating will increase with material thickness eventually preventing deposition by heating the grown material so that saturation of the solution along the interface cannot take place [29].

The amount of source material used in a LPEE experiment also dictates possible growth thickness. More source material allows for thicker growth. However, a large amount of source can lead to Joule heating issues. If the current is passing through the source, there will be excessive heating of the source that will lead to strong convection. This disrupts electromigration producing a less favorable interface shape and slower growth rate.

The final concern is grown crystal diameter. The need for perfect electrical contact between the back of the seed and substrate becomes an even greater concern with large diameter seeds required for device applications. The larger area makes the perfect contact required for high quality growth more difficult to obtain. In addition, LPEE should take place in an isothermal environment. A large diameter apparatus will have pronounced radial thermal gradients. This problem will be compounded when using a low thermal conductivity material like CdZnTe. Thermal gradients will disrupt the electromigration mechanism.

2.4.4 Advantages

2.4.4.1 Defect Density

LPEE growth is associated with very low impurity concentrations. Also, LPEE growth is free from growth striations and terracing. The grown material has been found to possess very low dislocation densities, usually under $10^3 cm^{-2}$. Dislocations will migrate from the seed into the grown material. This makes LPEE dependant on the quality of seed material. The combination of above properties makes LPEE grown material superior to material grown by other techniques [66].

2.4.4.2 Temperature and Composition

As a solution growth technique, LPEE has the advantage of growth taking place at temperatures well below melting. Growing from solution also allows segregation problems to be avoided. In the case of CdZnTe, zinc segregation is a major problem in melt growth techniques [61, 67, 68, 69]. Lower growth temperature avoids vapor pressure issues with constituent species. It also reduces defects caused by thermal stress during the cooling of the material. Finally, the cost of the apparatus is reduced by utilizing a lower growth temperature and avoiding the pressurized systems necessary to control evaporation in melt growth.

2.5 Cadmium Zinc Telluride

Cadmium Zinc Telluride, CdZnTe, is a type II-VI ternary semiconductor. It is a relatively new material being produced for both device and substrate uses. The material's electronic properties make it very attractive for new device technology. However, the material is very difficult to produce with current commercial techniques [1, 2, 3, 4, 5, 6, 7].

2.5.1 Crystal Growth

CdZnTe is produced commercially by both Czochralski and Bridgman techniques [28, 70]. These are both melt growth techniques and involve temperatures over $1050°C$. In both techniques, due to the low vapor pressure of species, especially cadmium, steps have to be taken to limit evaporation. Allowing evaporation will change the composition of the melt and those changes will be reflected in the grown material. The common solutions are inert gas over-pressure, cadmium over-pressure and encapsulation [71, 72, 73, 74, 75, 76]. Inert gas over-pressure uses a very high pressure, $100 atm$ or more, inert gas environment over the melt. This reduces evaporation by limiting the mean free path above the melt. Cadmium over-pressure works by saturating the atmosphere above the melt with cadmium. Excess cadmium is added to produce this effect. Cadmium is used as it has the lowest vapor pressure of the three species and preferentially evaporates [77]. An encapsulant can also be used to prevent evaporation loss. This is usually boron oxide, which provides a liquid covering of the melt free surface inhibiting evaporation. All these solutions, especially the pressure dependant ones, add significant cost to the experimental apparatus [78].

In melt growth of CdZnTe, zinc segregation is another major issue [79, 80, 81, 82]. As the material solidifies, the tendency is for the Zn concentration to change. This makes producing large amounts of material with uniform composition very difficult. The changing composition leads to mechanical stress and other defects in the grown material. The electronic properties of the material are also unfavorably impacted.

CdZnTe has low thermal conductivity. This makes a flat solidification interface during freezing very difficult to achieve. Therefore, melt growth material often has radial composition uniformity issues [83, 84].

Crystalline CdZnTe has low critical resolved shear stress values. This means it is prone to cracking especially during the thermal stress of cooling.

Given all these difficulties with melt growth, some producers have started using the travelling heater method to produce material. This techniques is prone to inclusions and other material defects arising from difficulties with moving the solvent zone. In addition, the yields from this technique are small when compared to melt techniques [47, 49, 51, 85, 86, 87].

2.5.2 Devices

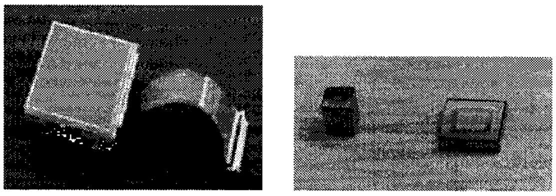
2.5.2.1 Infrared Detectors

The largest market for CdZnTe is a substrate for HgCdTe layers. The composition for this application is $Cd_{0.96}Zn_{0.04}Te$ [13, 14, 15]. Another commonly used substrate for HgCdTe is CdTe. However, $Cd_{0.96}Zn_{0.04}Te$ offers a better lattice match and superior substrate strength. This leads to higher quality device layers. Material availability has led to high material cost , which has limited CdZnTe use in this market [7, 8, 9, 10, 11, 12].

2.5.2.2 X-Ray and Gamma Ray Detectors

The other major application for CdZnTe is as a gamma-ray and hard x-ray detector. For this application the material is particularly well suited. It has a large absorption coefficient due to its constituent species, high atomic numbers and wide band gap suitable for high energy photon detection. The primary response wavelength is tunable by varying the percentage of zinc in the ternary. This allows tailoring of the detector to the application. Typical compositions include $Cd_{0.90}Zn_{0.10}Te$ and others with higher Zn percentages [16, 17, 18, 19, 20].

The most attractive feature of CdZnTe based detectors is their operating temperature. A CdZnTe detector will be able to operate at around room temperature. This is in dramatic contrast with current detectors in commercial use, which require cryogenic temperatures. In the medical imaging field, the use of CdZnTe based detectors could significantly reduce the cost of a gamma ray imaging system by negating the need for cryogenics [22, 21, 23]. Currently, CdZnTe gamma ray and hard x-ray detectors are available. Their physical size is still limited due to production issues. Some examples of CdZnTe detectors are shown in Figure 2.16.



(a) HgCdTe IR Detector.

(b) Two simple CdZnTe based gamma ray detectors.

Figure 2.16: Photos show examples of CdZnTe based Detectors. The infrared detector uses CdZnTe as a substrate.

2.5.3 Thermodynamic Properties

The phase diagram for CdZnTe is not well investigated. Few examples exist in literature [88, 89, 90, 91, 92]. The most common treatment is to consider the ternary as a quasi-binary system. The quasi-binary components are cadmium telluride, CdTe, and zinc telluride, ZnTe. The lack of phase diagram information complicates the solution preparation for LPEE.

CdZnTe has low thermal conductivity values [93, 94]. This produces difficulties in growth from the melt. It makes keeping the interface flat a challenge. A shaped interface will result in radial compositional gradients.

CdZnTe displays another interesting behavior in the melt. In its liquid form, the cadmium and zinc do not fully dissociate from their paired tellurium [95]. In a stoichiometric CdZnTe melt, the species found are mainly CdTe and ZnTe. In a dilute solution like the LPEE solution, there are mainly CdTe, ZnTe and solvent Te.

2.5.3.1 Vapor Phase

One of the most important considerations are the species vapor pressures. Cd and Te have low vapor pressures [96, 97, 98]. Cadmium is especially troublesome. During an experiment in an open container Cd will be preferentially lost. In melt growth, this can cause compositional variations in the grown material. In solution growth there can be problems keeping the solution saturated [99]. Tellurium's vapor pressure is also low and is lost along with the cadmium. In solution growth, where Te is in excess, tellurium will be lost at an accelerated rate. Taking advantage of this, crystals are now being prepared using a solvent evaporation technique where the tellurium solvent is allowed to completely evaporate leaving a CdZnTe crystal behind [100].

In addition to the evaporation issues, solid CdZnTe sublimates at relatively low temperatures [101, 66, 102]. To quantify the extent of this process, a substrate was heated to $800°C$ and held there for twenty-four hours. The amount of material lost can be seen in Figure 2.17.

2.5.3.2 Synthesis

It has been noted that synthesizing CdTe, ZnTe and CdZnTe is a problematic process. During the compounding process, the elements react in an exothermic fashion. This reaction can be quite violent and results in splashing and heavy evaporation. The synthesis process needs to be well managed to avoid unpredictable results [101, 103, 104].

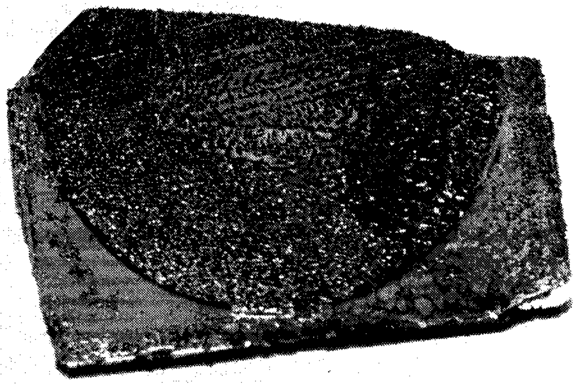


Figure 2.17: Sublimation damage to a 2.5mm CdZnTe Substrate. The center circular area was open to the hydrogen environment for twenty-four hours at growth temperature. The other areas were covered by part of the crucible. The substrate lost 0.25mm of height and 2.26g of weight over the course of the experiment.

2.5.4 Physical Properties

Table 2.1 summarizes some properties of CdZnTe. Some are dependant on the relative amount of Zn in the ternary.

Table 2.1: General Properties of CdZnTe [19, 89, 105].

Structure:	Zinc-Blende
Lattice Parameter:	$0.64652nm$ (4% Zn)
Band Gap:	$1.56eV$ (4% Zn)
Mobility, Electron:	$1050cm^2V^{-1}s^{-1}$
Mobility, Hole:	$100cm^2V^{-1}s^{-1}$
Dielectric Constant:	10.2
Partial Pressure:	Cd, 13.6×10^5 Pa (14% Zn at 1080°C)
	Zn, 1.6×10^5 Pa (14% Zn at 1080°C)

Section 3

Experimental Results

3.1 Apparatus Design

The LPEE apparatus used in this study was originally developed for LPEE growth of GaAs and GaInAs. The apparatus proved highly successful for growing these materials. In this study, we began using the GaAs crucible as is and used our initial experiments to identify design issues.

3.1.1 Apparatus Description

The basic LPEE apparatus is very simple. This fact makes an LPEE system relatively inexpensive when compared with other techniques. The system at the University of Victoria is built around a Mellen Company vertical, 2.5 inch diameter tube furnace. This furnace is designed for operation inside a magnetic field. Operating in a magnetic field, while not performed in this work, is necessary to obtain the yield that makes LPEE a bulk growth alternative. The furnace is supported on an aluminum platform adjustable in height. An aluminum flange is suspended from the wall over the furnace bore. The wall mount was chosen to minimize the effect of vibration generated by the magnet's helium compressor. This flange supports the crucible and reaction vessel. It is water cooled to prevent overheating of the quartz–aluminum seal, which uses a Viton o-ring. The setup is shown in Figure 3.1

Hydrogen is provided to the flange by way of a gas board. The board includes a flowmeter on the inlet side and a bubbler on the outlet side. This allows for easy setting of the gas flow. The hydrogen passes through a moisture trap and an oxygen trap before entering the system. Pressure gauges on the inlet and outlet lines, with over-pressure release valves, complete the gas board. The board is shown in Figure 3.2. Gas is provided from a hydrogen cylinder. Two cylinders are connected to the system at a time, the second as a reserve, to ensure an uninterrupted supply of hydrogen.

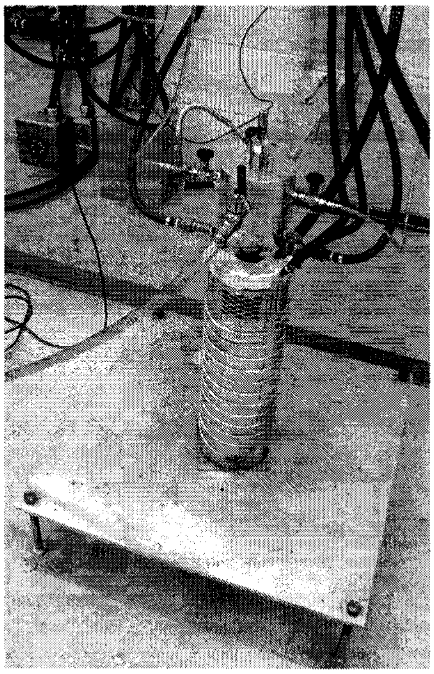


Figure 3.1: Photo showing the aluminum flange suspended from the wall over the furnace and stand. Hydrogen, cooling water and vacuum lines are evident.

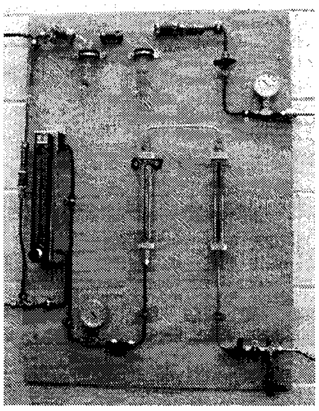


Figure 3.2: Gas Board.

The system can be put under vacuum utilizing a two stage vacuum system. There is a rotary vane rough pump and a turbomolecular pump. This system is necessary to ensure minimal contamination to the hydrogen environment.

The current is provided by a $1kW$ DC current source. The source leads are connected to suitable power terminals by way of heavy cable and split bolt connections.

3.1.1.1 Temperature Profile

The temperature profile required for optimal LPEE growth is an isotherm over the length of the crucible. The three-zone design of the furnace allows this profile to be well approximated. Each zone is independantly controlled. The controller is shown in Figure 3.4. The normal conditions for an adequate temperature profile is the substrate to be at growth temperature, the source to be within $2-3°C$ of growth temperature and the solution prep-well to be within $5-6°C$ of growth temperature. A typical profile is shown in Figure 3.3. The experiments in this study were conducted under these profile conditions. The profile conditions could be improved to a better isotherm by the use of a heat pipe. Unfortunately, the space requirements do not allow for use of a heat pipe in the current furnace.

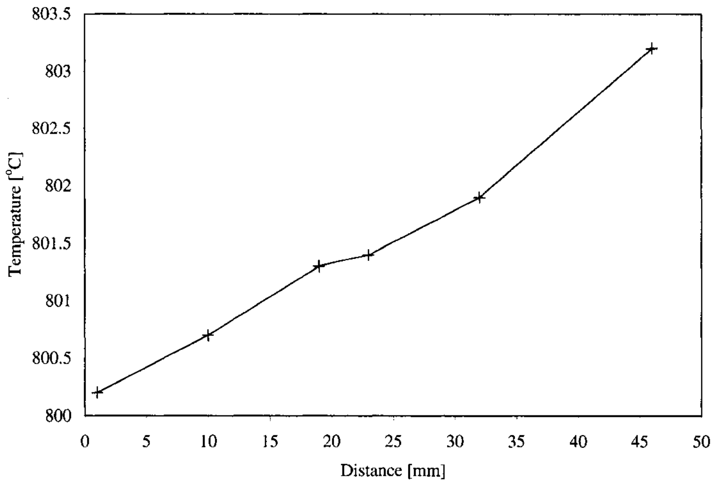


Figure 3.3: Typical growth temperature profile. $0mm$ indicates the middle of the substrate. $45mm$ indicates the middle of the solution preparation well. The temperature difference from substrate to source is approximately $0.75°C$

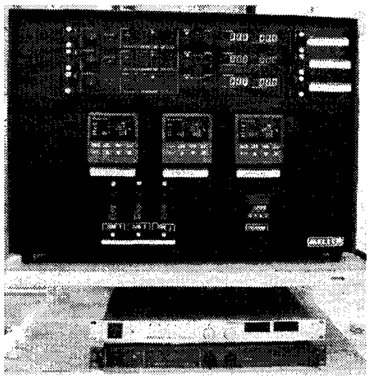


Figure 3.4: Photo of the 3 zone furnace controller. Below are two $1kW$, $8V$–$125A$, DC current/voltage sources.

3.1.2 Crucible Description

The LPEE crucible developed during this work is illustrated in Figure 3.5. The crucible functions as follows. The solution is prepared for growth above the source and substrate. It is gravity fed into the growth environment the solution is determined to have saturated.

The source is suspended above the substrate in a graphite holder. The solution preparation well, also graphite, and the source holder act as the upper electrode in the system. The source holder allows the current to bypass the source, which avoids excess Joule heating [29]. The growth solution is contained in a pyrolytic boron nitride cylinder. The top is formed by the source and the bottom is formed by the substrate. The substrate is held above the bottom graphite electrode with a boron nitride holder.

The gap between the substrate and electrode allows for a liquid contact zone. The contact zone gap is eliminated when using a solid contact zone. The crucible is hung in the furnace using molybdenum rods.

The entire setup is contained within a quartz reaction vessel. Hydrogen is circulated in the reactor during experiments. The DC current source used to drive the growth process is connected to the crucible electrodes by molybdenum rods.

3.1.3 Material Interactions

One of the initial problems discovered was material sticking to crucible surfaces. The porous nature of the graphite used in the solution preparation well allowed material to bind to the walls and not drop when the well plug was released. A similar problem arose with the source holder. Material would bind to the graphite and make removing the grown crystal very difficult [106].

The problem of material sticking to the graphite well was resolved by using a quartz insert to cover the graphite walls. This prevented further

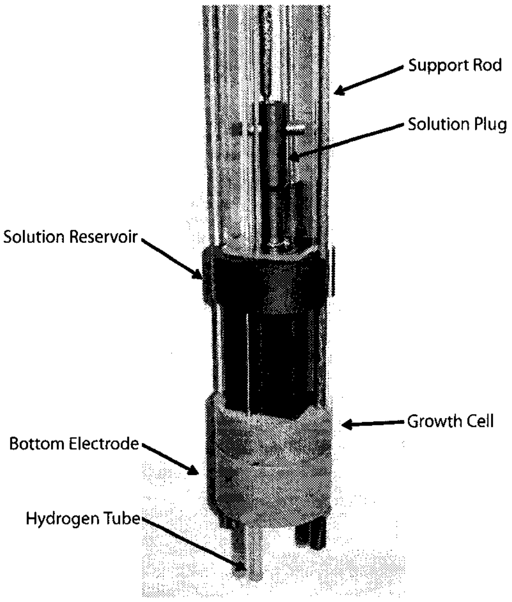


Figure 3.5: Photo of the LPEE crucible assembled and hanging from its molybdenum support rods. The hydrogen supply tube is evident. It passes through the crucible and terminates past the lower edge of the crucible.

sticking issues. In addition, new parts were machined from a higher quality, low porosity graphite. This helped alleviate sticking issues on graphite surfaces exposed to solution. Using a pyrolytic graphite coating on the surfaces was also investigated. Due to high cost and the evolving nature of the design, this option was not pursued. However, it would be an excellent solution once a final design is reached. Experiments were conducted with a sample of coated graphite, which performed excellently. In addition, the pyrolytic boron nitride cylinder used as the growth well has no sticking issues.

Another major issue was the interaction of the material vapors and the molybdenum rods. The material vapors caused severe corrosion of the rods. This is illustrated in Figure 3.6. The damage resulted in problems when removing the crucible after an experiment and dramatically shortened the lifetime of the rods. The crucible removal issues were solved by a complete redesign of the rod system. All connections were removed from the hot zone of the furnace and moved away from the effect of the material vapors. The lifetime issue was also addressed. The rods were sheathed with quartz tubing. This solution leaves some molybdenum still exposed, which is subject to corrosion. However, it extends the life of the rods significantly. Other materials were considered, including graphite, but it was decided to continue to use molybdenum as the problem was manageable in the scope of a feasibility study.

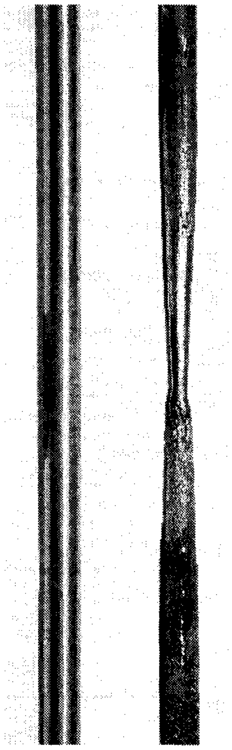


Figure 3.6: This photo compares an unused support rod, left, with a support rod after approximately eight experiments. The corrosion is clearly evident.

3.1.4 Leakage

Solution leakage proved to be an issue with the crucible. The nature of the crucible is such that there are many interlocking parts. The GaAs solution is a relatively high viscosity fluid. It would not leak through the seams between crucible pieces. The CdZnTe solution proved to be able to readily leak between parts [107]. Leakage between the parts is very problematic as it results in loss of electric contact between the source and substrate and termination of growth. In addition, solution leakage will damage and destroy crucible parts. Sealing crucible parts together is not an option. The grown material has to be easily extracted, and the differing materials used in the crucible means allowance for differing thermal expansions has to be considered.

This issue was solved by improving the seal between the crucible pieces where possible. In addition, the pieces are now pressed together once growth temperature is reached. This prevents any seams opening during the experiment. All sealing surfaces are cared for carefully to avoid any damage. Leakage will still occur if the substrate is broken or dissolved during the experiment.

3.1.5 Other Adjustments

The last major change to the crucible was to use a lid over the solution preparation well. This helped limit contamination to the solution from any impurities that could drop in during the loading process or experiment. In addition, it was thought that a lid could help slow the evaporation process. Other small changes introduced in the new crucible were made to ease machining, reduce material consumption and improve part lifetime.

The electrical connections at the upper and lower electrodes were completely redesigned. The new system significantly improves the reliability of the connections, which had been problematic in the GaAs crucible.

Some apparatus changes were also introduced. Hydrogen circulation was improved in the reaction vessel. Hydrogen is now circulated from an inlet below the crucible to an outlet above. The gas is pre-heated as it travels down a tube through the furnace hot zone. This helps keep the isothermal profile over the crucible. The gas flow aids in removal of impurities and other volatile components from the growth environment.

The seal of the quartz reaction vessel to its aluminum flange was also changed. The new design improves the quality of vacuum that can be achieved and therefore the purity of the hydrogen environment. In addition, the new seal is more reliable keeping the growth environment isolated during experiments.

3.2 Preparation Procedure

For high quality, defect-free material careful experiment preparation is required. Detailed descriptions of all the procedures mentioned here are included in Appendix A.

3.2.1 Apparatus Cleaning

All materials involved in the apparatus are cleaned prior to an experiment. The aluminum flange and quartz seal parts are all wiped with methanol. All o-rings are cleaned with methanol. Any corrosion is mechanically removed from the molybdenum parts. All molybdenum and other metal parts are washed in acetone followed by a wash in methanol. The quartz reaction vessel and other quartz parts are chemically etched with aqua regia.

The crucible parts are similarly cleaned. All ceramic parts, boron nitride and graphite, are carefully wiped clean. Any hard deposit is removed mechanically. Contact with any liquid is avoided due to the porous nature of the materials. All ceramic parts are occasionally washed, every few experiments, with de-ionized water and methanol in an ultrasonic washer. They are then baked to remove any traces of water. The pyrolytic boron nitride cylinder and quartz solution insert are etched with aqua regia. The quartz insert is additionally etched in hydrofluoric acid. All parts are stored in a desiccator between experiments to reduce moisture content and contamination.

3.2.2 Material Cleaning

The materials all require cleaning prior to loading the experiment. In a typical experiment, we use a CdZnTe substrate and source. These are chemically etched using a 5% bromine, 95% methanol solution [108]. For the solution material, the materials are CdTe, ZnTe and Te. The CdTe and ZnTe are etched using the bromine methanol solution. The Te is supplied in bags sealed under argon. The Te is used as is and is taken from its packet just before loading. The CdTe and ZnTe that were used were both 5N materials. Both 5N and 6N qualities of Te were used in these experiments.

In addition to the materials above, various contact materials were used during experiments. Cadmium and zinc were also used in some experiments. All of these materials were appropriately chemically etched.

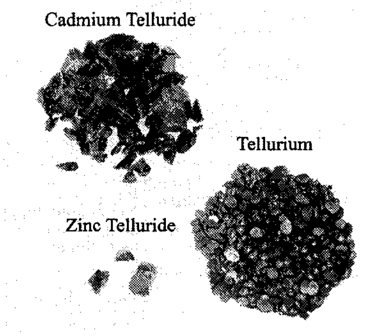


Figure 3.7: Typical quantities of materials for the LPEE solution prior to loading. 1g ZnTe, 27g CdTe ,and 30g Te.

3.2.3 Crucible Loading

Following material cleaning, the crucible was quickly loaded to minimize time in the room environment. All materials are carefully dried using compressed nitrogen. In the case of a liquid contact zone, it has to be pre-melted before adding the substrate. This is illustrated in Figure 3.17 and 3.9. Melting this material in the room environment introduced oxides into the contact material. Unfortunately, this was unavoidable given design constraints. Once the material is loaded, the crucible is hung from the aluminum flange such that it is at the proper position within the furnace. The system is then sealed within the quartz reaction vessel.

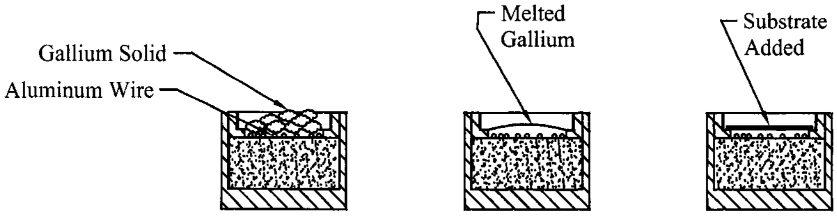
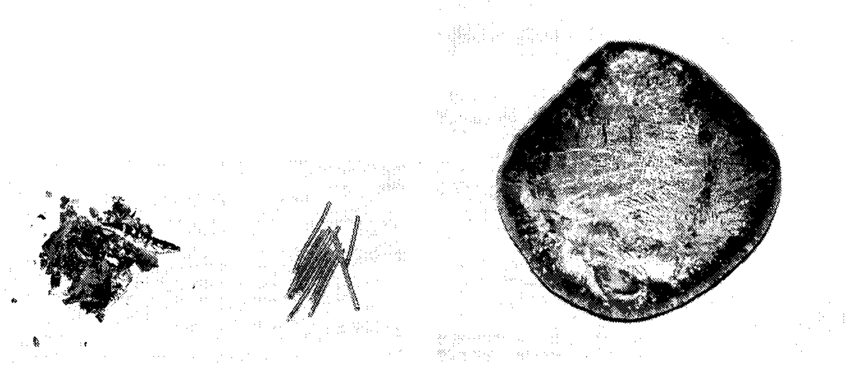


Figure 3.8: Illustration of liquid contact zone preparation.

The sealed reaction vessel is vacuumed until a pressure of approximately 10^{-5} *mbar* is reached. The system is then purged three times with hydrogen. Between each purge the system is pumped back down to the starting pressure. The hydrogen used in these experiments is an ultra high purity grade. After the final purge, the system is filled with hydrogen and an outlet is opened to start the gas flow. The hydrogen is allowed to flow for the duration of the experiment.

3.2.4 Experiment Procedure

The system is careful brought to growth temperature. The first step in heating is to raise the temperature to 300°*C*. The system is left here for a time to



(a) (b)

Figure 3.9: Photos show contact material preparation. Photo (a) shows the gallium and aluminum prior to pre–melting. Photo (b) shows the pre–melted materials. The oxide skin on the melted materials is evident.

help clear any residual water vapor. The system is then very slowly heated, approximately $50°C$ per hour, to growth temperature. The heating rate is kept low to avoid a strong reaction in the solution. As previously mentioned, the solution undergoes an exothermic reaction during compounding at around $450°C$. A slow heating rate helps to keep this reaction from happening too fast and causing material to splash.

When growth temperature is reached, the system is allowed to sit undisturbed so the solution can fully saturate. Once this period is finished the well plug is removed and the solution drops into the growth cell. A short period is then allowed for the system to move towards equilibrium. Finally, the electric current is applied. When the desired growth duration has passed, the current is shut off. The system is then carefully cooled at a rate of about $50°C$ per hour. The slow cooling helps avoid thermal stresses in the grown material.

3.2.4.1 Current Density

All the experiments performed in this study used the relatively low current density of $3Acm^{-2}$. This was chosen to minimize Joule heating in the system, which can lead to growth problems. The low current density will slow growth, but it will show the feasibility of this technique. Current densities up to $10Acm^{-2}$ have been used in the GaInAs LPEE system.

3.3 Experiment Results

After the initial experiments to identify problem areas, a systematic approach to the problems was used. The first area investigated was the interaction between the contact zone materials and the substrate. This was followed by an investigation of the solution-substrate interaction. Finally, the entire system was tested again to initiate growth.

3.3.1 Contact Zone

The contact zone is one of the most important considerations in the LPEE system. The electrical contact must be as uniform as possible to ensure even growth across the substrate. In addition, the contact zone must allow for easy extraction of the grown material. The contact experiments are summarized in Table 3.1.

Table 3.1: Details of experimentation with contact zone types. Good Contact indicates that uniform contact was achieved. Substrate Lost Indicates the substrate was dissolved.

Experiment Number	**Substrate**	**Contact**	**Duration [Days]**	**Result**
CZT10	CdZnTe, 3mm poly	Ga–Al, 10% Al	3	Substrate Lost
CZT11	GaAs, 0.5mm	Ga–Al, 10% Al	3	Substrate Intact
CZT12	GaAs, 0.5mm	Al	1	Substrate Intact
CZT13	CdZnTe, 2.5mm poly	Ga–Al, 10% Al	1	Good Contact
CZT14	CdZnTe, 2.5mm poly	Ga	1	Substrate Lost
CZT15	CdZnTe, 2.5mm poly	Ga–Al, 20% Al	1	Substrate Lost
CZT17	CdZnTe, 5mm poly	In	1	Substrate Lost
CZT18	CdZnTe, 2.5mm poly	Ga–Al, 10% Al	1	Good Contact
CZT19	CdZnTe, 2.5mm poly	Ga–Al, 10% Al	3	Substrate Lost

Table 3.1: Details of experimentation with contact zone types.

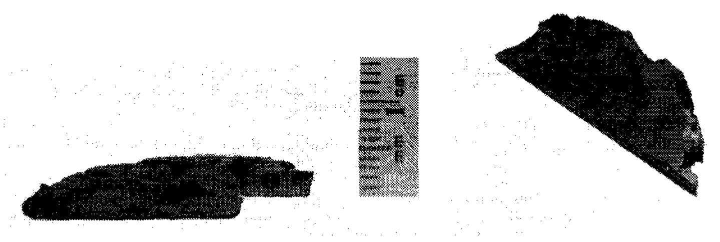
Experiment Number	**Substrate**	**Contact**	**Duration [Days]**	**Result**
CZT22	CdZnTe, 2.5mm poly	Ga–Al, 15% Al	3	Good Contact
CZT29	GaAs, 0.5mm	Ta Foil	1	Foil Oxidized
CZT48	CdZnTe, 1.27mm	Al Foil	2	Foil Oxidized
CZT49	CdZnTe, 1.27mm	Al Foil	3	Foil Oxidized

3.3.1.1 Liquid

In the GaAs LPEE system, a mixture of gallium and aluminum was the contact material of choice. The material melted easily at low temperature. This allowed for easy loading of the substrate and removal of the grown crystal. The mixture had little effect on the GaAs substrate, just dissolving the back slightly, which actually helped form a better contact by removing surface damage and contamination [29].

The effect of the gallium-aluminum mixture on the CdZnTe substrate was dramatically different. The contact material aggressively dissolved the substrate. This was seen in experiments CZT10, CZT14, CZT15 and CZT19. In addition, a new compound is formed when the two materials mix. This was first noticed during the initial experiments when the solution and contact material mixed. A hard compound formed that bound to the crucible surfaces. An example of this is illustrated in Figure 3.10.

During the testing of the GaAs contact zone, it was found that increasing the aluminum content in the mixture suppressed the gallium from dissolving the substrate. This same line of testing was followed with the CdZnTe, various ratios of Ga and Al were tried. The original composition was approximately 10% Al and 90% Ga an was tried in CZT10, CZT13, and CZT19. By changing this to 20% Al and 80% Ga in CZT15, acceptable levels of back dissolution were hoped to be achieved. However, problems persisted with the liquid contact. The results when using this material were inconsistent. In experiment CZT15 the contact completely dissolved the substrate and in CZT22 good contact was achieved. It seemed that factors such as how the two constituents mixed were affecting the interaction with the substrate.



(a) CZT15, Cross Section (b) CZT15, Top

Figure 3.10: Photos show the result of a contact zone test using a 20% aluminum, Ga–Al mixture. The substrate has completely mixed with the contact material.

At this point other materials were considered. Indium was tried but had the same effect as gallium. Low melting temperature materials were required due to the loading procedure. The contact zone must be molten before the substrate is added. Any solid in the contact zone could cause the substrate to break. This severely limits our material choice. To allow even higher amounts of aluminum to be used in the mixture and avoid substrate breakage, a reservoir system was devised to allow the contact zone to be melted during heating rather than prior to loading. Problems existed with this apparatus as the contact material interacted with the quartz tubes used to deliver the contact material causing damage. In addition, the substrate interaction remained inconsistent. The reservoir system would allow new higher temperature contact materials to be used. However, as this work is a feasibility study the decision was made to continue with the gallium-aluminum system, rather than try to investigate the vast variety of other materials available.

Another benefit of a reservoir system is that it allows for perfect filling of the contact zone. In the current loading system, precise amounts of material have to weighed in order to generate the correct volume of liquid. Too much material will put pressure on the substrate and can lead to breakage. Too little material will result in inadequate electrical contact. A reservoir system would eliminate this issue. Excess contact material could always be used.

The inconsistency of the contact-substrate interaction was thought to stem from problems with how the two materials, Ga and Al, were mixing. A few premixing options were investigated. The first involved casting the gallium-aluminum mixture prior to loading the experiment. The materials were heated to well above their melting temperatures in a hydrogen environment. The mixture was allowed to mix for a period of time at this temperature. Finally, it was quickly quenched in ice water. Unfortunately, problems arose when trying to process the material. The gallium and aluminum form a eutectic structure on solidification. Cutting this material was impossible as the gallium would melt out of the eutectic with the heat from the blade of the saw, even when water cooled. This problem could be solved by trying to shatter the material after cooling it to a low enough temperature. Another issue was cleaning the material. Chemical etching was not an option as chemical etches for aluminum did not effect the gallium and chemical etches for gallium completely dissolved the aluminum. Given the amount of handling the cast material will experience, a good cleaning method is essential.

Another premixing technique was to contain the contact material in a reservoir with a plug until it was completely mixed, then introduce it into the contact zone. This setup is similar to the system used for LPEE solution. While this system successfully premixed the material, its complexity made its performance unpredictable. The apparatus is illustrated in Figure 3.11.

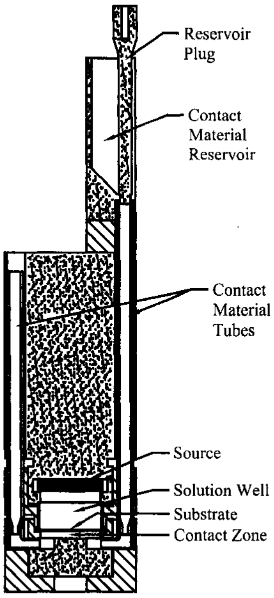


Figure 3.11: Diagram of contact reservoir system developed to pre-mix contact material and facilitate melting inside the furnace.

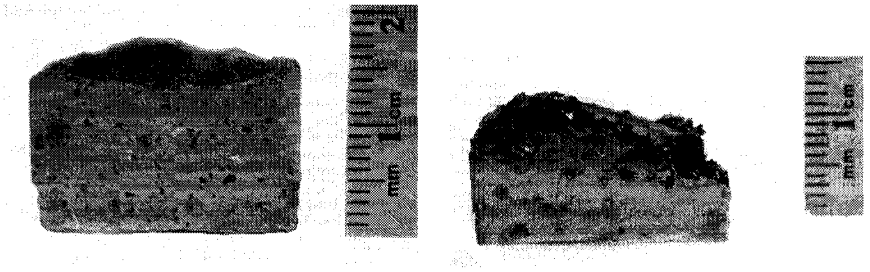
The final decision on the liquid contact was to use the 15% Al and 85% Ga mixture. This contact minimally back-dissolved the substrate over 3 days, illustrated in Figure 3.12. Lower aluminum percentages fully dissolved the substrate over the 3 days, illustrated in Figure 3.13. Higher aluminum

(a) CZT13 (b) CZT18

Figure 3.12: Photos show successful contact tests where minimal back etching took place. There was no solution introduced in these experiments. The top of the substrate remained exposed to the hydrogen environment.

percentages caused damage to the graphite electrode and seemed to suffer severely from mixing issues. Since the reservoir system did not perform perfectly and added a lot of complexity, it was decided to stay with the original loading procedure. This system performed the best of the liquid contacts.

The testing of the liquid contact zone was conducting without any solution in the growth cell. When solution was added to the experiment the substrate was consistently lost to dissolution. This is despite both the contact material and solution not having an adverse effect when in the system alone. The conditions created when there are liquid zones on either side of the substrate seem to aid in dissolution of the substrate. Due to this problem, non-liquid contact zone options were investigated.



(a) CZT30 (b) CZT52

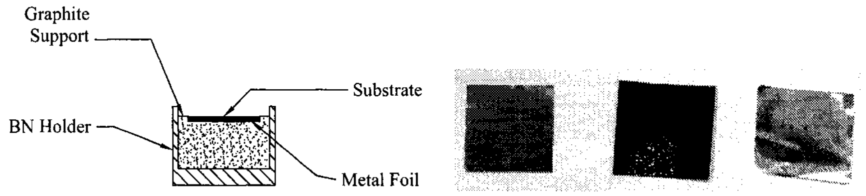
Figure 3.13: The photos above illustrate experiments where the contact zone and solution have mixed. No evidence of the substrate can be seen. This result occurred whenever the liquid contact was used in conjunction with the solution.

3.3.1.2 Solid

The numerous difficulties with using a liquid contact made other options very attractive. One option was to use a solid type contact zone. This type has been used in other LPEE experiments [31, 32, 55, 56]. In these experiments, an inert metal foil, tantalum or platinum, is placed between the substrate and the electrode. The faces of the foil are wetted with liquid gallium to ensure perfect contact. This system is indicated in Figure 3.14. In our experiments, numerous difficulties were found with this system. In particular, there were issues with the foil oxidizing and disrupting contact. It is unclear whether this is from material issues or inadequate vacuum.

A similar system tested was to melt a thin sheet of aluminum between the substrate and electrode. The molten aluminum would fill any surface imperfections and ensure perfect contact. The electrode and substrate would be stuck together at the end of the experiment. This problem was avoided by changing the electrode design, such that it is thin graphite backer that is stuck to the substrate. This backer is then lost with the experiment. The same issue that plagued the other foils plagued this system as well. The aluminum foil oxidized on heating rather than melting.

The contact solution that proved to be the most successful, was to use a graphite suspension as the contact material. A suspension of fine graphite dust and methanol was prepared. The surface of the electrode and the back of the substrate were then brushed with the suspension. The two surfaces were then pressed together. This system will not provide as even a contact as a liquid zone. However, it produced more consistent results than the best liquid contact.



(a) Solid Contact

(b) Foils

Figure 3.14: The diagram on the left shows the basic setup for the solid contact system. The photo on the right shows the various foils tested in the experiments. From left to right they are Pt, Ta and Al.

3.3.2 Solution Preparation

Table 3.2: Details of experiments to find optimum solution preparation method. Insufficient solution indicates there was a lack of solution and no electrical current could be applied across the growth cell. Compound dissolution refers to the how the solvent tellurium interacted with the solute CdTe and ZnTe.

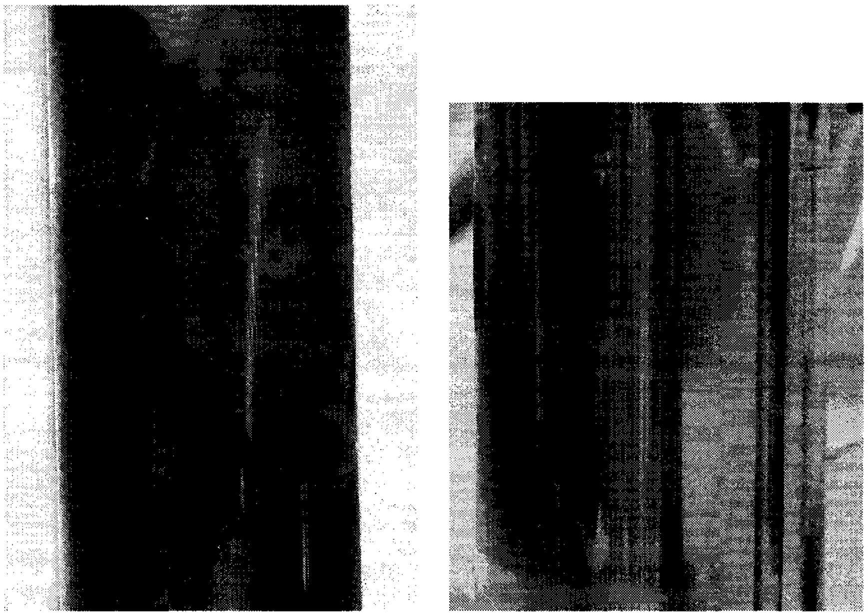
Experiment Number	**Substrate**	**Solution**	**Duration [Days]**	**Result**
CZT23	Graphite	Elements, 75% Te	1	Insufficient Solution
CZT24	Graphite	Elements, 75% Te	1	Insufficient Solution
CZT25	Graphite	VGF CdZnTe, 75% Te	1	Insufficient Compound Dissolution
CZT27	Graphite	VGF CdZnTe, 75% Te	1	Good Compound Dissolution
CZT28	Graphite	VGF CdZnTe, 75% Te	3	Good Compound Dissolution

Table 3.2: Details of experiments to find optimum solution preparation method.

Experiment Number	**Substrate**	**Solution**	**Duration [Days]**	**Result**
CZT31	CdZnTe, 2.5mm poly	VGF CdZnTe, 75% Te	1	Insufficient Solution. Substrate Intact.
CZT34	CdZnTe, 2.5mm poly	VGF CdZnTe, 75% Te	3	Insufficient Solution. Substrate Intact.
CZT36	CdZnTe, 1.27mm	CdTe & ZnTe, 75% Te	1	Insufficient Solution. Substrate Intact.
CZT38	CdZnTe, 1.27mm	CdTe & ZnTe, 80% Te	3	Insufficient Solution. Substrate Intact.

The preparation of the solution for growth was another well investigated part of the growth system. The experiments are detailed in Table 3.2. The first concern was growth temperature. The GaAs LPEE growth temperature was $800°C$. As GaAs experiments were ongoing during this work, $800°C$ was chosen as the growth temperature for continuity. A lower temperature may be more appropriate for CdZnTe growth due to its vapor pressure issues. However, as this was a feasibility study an $800°C$ growth temperature would provide adequate results.

The first few LPEE experiments used elemental materials to prepare the solution, experiments CZT23 and CZT24. Cadmium, zinc and tellurium were placed in the solution preparation well to compound and form the solution. A number of problems were noted with this procedure. During heating, there was a tremendous material loss due to evaporation. In addition, a solution did not always form from the elements. In some experiments, the material would form a solid porous mass. These issues were attributed to the compounding reaction taking place as the solution formed. The problem was alleviated by avoiding the compounding reaction. This was achieved by using CdTe and ZnTe instead of Cd and Zn alone [15]. Tellurium alone was still added to act as the solvent. During heating, the CdTe and ZnTe are dissolved by the Te until equilibrium is reached. Initially, CdZnTe from the Vertical Gradient Freeze experiments was used as the solution material to test the method. To improve consistency, the material was later switched to commercially available CdTe and ZnTe. The difference the switch from elements to compounds made to material evaporation is illustrated in Figure 3.15.

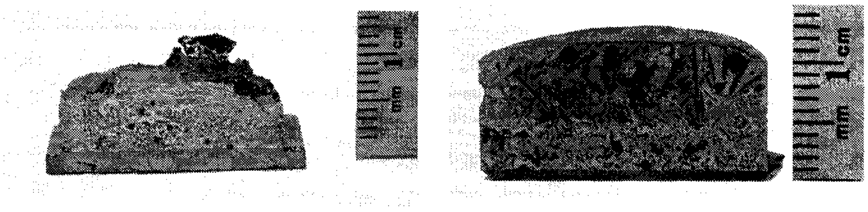


(a) (b)

Figure 3.15: Two photos of material deposition on the quartz reactor tube. Photo (a) shows the deposition before switching to using compounds for the solution synthesis. The reactor tube is opaque with material. Photo (b) shows the deposition when using the compounds, CdTe and ZnTe, for the solution. The support rods are now clearly visible through the glass.

Another issue with the solution, which was not resolved, was its volume. Due to the expense of all the materials and to ensure easy extraction of any grown material, solution volume should be kept to a minimum. This proved difficult as proper control of the solution volume was never achieved. The amount of solution generated from the starting materials fluctuated over the experiments and caused numerous failed runs.

The substrate-solution interaction was tested thoroughly. Specifically, the ability of the solution to saturate and stay saturated during the growth process was investigated. First it was confirmed that the solution was satu-



(a) CZT34 (b) CZT36

Figure 3.16: Stability of solution–substrate system.

rated prior to its introduction into the growth cell. This was accomplished by running short experiments. The solution was dropped onto the substrate and allowed to stay there for a length of time with no electric current. The system was then quenched. By looking at the substrate-solution interface and at the amount of un-dissolved solid left in the solution preparation well, the saturation of the solution was gauged. This is illustrated in Figure 3.16.

It was found that once growth temperature was reached, a lengthy period of time was required for the solution to fully saturate. In addition, excess CdTe and ZnTe over the ratio required for a saturated solution was required. This excess material helped replenish material lost to evaporation. The ability of the solution to stay saturated was tested by conducting the same tests over longer periods of time. It was found that with an initially saturated solution, there was no issues with the solution prematurely diluting due to evaporation. This is likely due to the much smaller free surface open to the hydrogen environment once the solution is in the growth cell. The longevity tests were conducted without source material to more accurately gauge saturation.

The solution staying saturated is a particularly good result. The LPEE crucible is inherently an open system. It would be very difficult to adapt it to a cadmium overpressure type system and very expensive to use an inert gas overpressure system. The solution staying saturated shows that neither of those two systems is likely necessary for successful growth.

This was nicely illustrated in one experiment where there was a lack of solution volume. The material was left in contact with the substrate for forty-eight hours then slowly cooled. No electric current was applied. However, growth is evident on the substrate, illustrated in Figure 3.17. This is likely caused by the LPE process. This clearly indicates that the solution is staying well saturated.

Figure 3.17: CZT44 showing LPE growth.

3.3.3 Substrate Issues

The conclusion of the experimental work in this study was plagued by substrate issues. In the preliminary experiments thick polycrystal substrates were used to test various aspects. This substrate was chosen due to its much lower cost over single crystal seeds. The material had to be thicker to compensate for the brittleness of the polycrystal. In the final experiments, we switched to thinner single crystal substrates, shown in Figure 3.18. These substrates did not perform well.

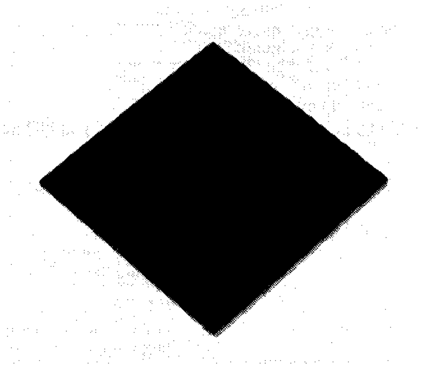


Figure 3.18: One of the 1.27mm single crystal substrates used in this study.

The graphite suspension contact zone no longer performed adequately with the thinner substrates. This led to islands of growth in some areas and complete dissolution in others. The effectiveness of this type of contact seems tied to the thickness of the substrate.

To achieve results with a single crystal seed, it was decided to try to use GaAs single crystal seeds [109]. The gallium arsenide seed is compatible with a liquid contact and should eliminate the contact zone issue. Unfortunately, the GaAs substrate dissolved when the CdZnTe solution was added. It appears that the CdZnTe solution is incompatible with the GaAs seed.

Using a thicker CdZnTe single crystal was not tried. This was due to time and cost restraints. It is possible that similar results to those achieved with the thick polycrystal substrate could be realized.

3.3.4 Source Material

The source material utilized throughout these experiments was 5*mm* thick polycrystalline CdZnTe, illustrated in Figure 3.19. The composition was $Cd_{0.96}Zn_{0.04}Te$. This matches the composition of the CdZnTe substrates used. From previous LPEE experience, it has been found that the source material determines the composition of the grown material[29].

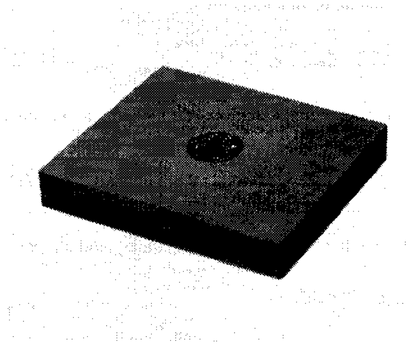


Figure 3.19: 5*mm* thick source material as used in this study.

3.3.5 LPEE Growth

Table 3.3: Conditions under which LPEE growth was successfully initiated.

Exp. No.	**Substrate**	**Source**	**Solution**	**Duration** [*Days*]	**Current** [$A\ cm^{-2}$]
CZT32	CdZnTe, 2.5mm poly	None	VGF CdZnTe, 75% Te	3	3

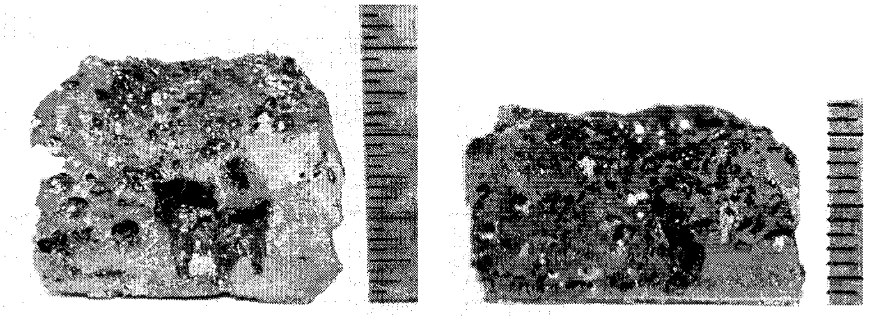
Table 3.3: Conditions under which LPEE growth was successfully initiated.

Exp. No.	**Substrate**	**Source**	**Solution**	**Duration** *[Days]*	**Current** $[A\ cm^{-2}]$
CZT33	CdZnTe, 2.5mm poly	None	VGF CdZnTe, 75% Te	3	3
CZT35	CdZnTe, 2.5mm poly	None	VGF CdZnTe, 75% Te	3	3
CZT37	CdZnTe, 1.27mm	CdZnTe, 5mm	CdTe & ZnTe, 80% Te	3	3
CZT39	CdZnTe, 1.27mm	CdZnTe, 5mm	CdTe & ZnTe, 82.5% Te	3	3
CZT40	CdZnTe, 1.27mm	CdZnTe, 5mm	CdTe & ZnTe, 80% Te	5	3

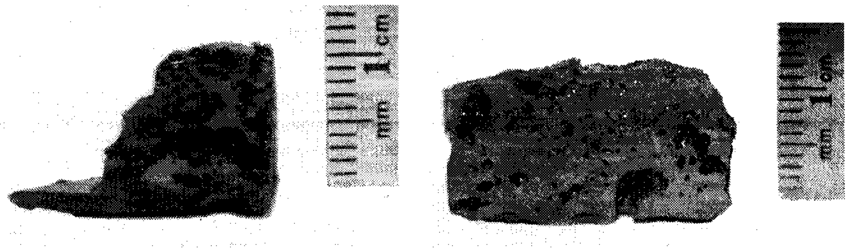
Table 3.4: Growth Experiment Results

Experiment Number	Result
CZT32	Growth initiated on part of solution–substrate interface. Island formation.
CZT33	Growth initiated across entire solution–substrate interface.
CZT35	Growth initiated across entire solution–substrate interface.
CZT37	Growth initiated on part of solution–substrate interface. Island formation.
CZT39	Growth initiated on part of solution–substrate interface. Island formation.
CZT40	Growth initiated on part of solution–substrate interface. Island formation.

Despite the difficulties encountered in almost every aspect of the growth system, LPEE growth was successfully initiated in a number of experiments. These are summarized in Table 3.4 and the experimental conditions in Table 3.3. The most common type of growth observed was island type. Island type growth is the situation when growth is initiated on only one section of the substrate. This occurs due to contact problems at the back of the substrate. The areas of the substrate where growth has not been initiated usually dissolve. With all the issues concerning the contact zone during these trials, it is no surprise that island growth was the most common growth observed. The results of island growth are shown in Figure 3.20.



(a) CZT37 (b) CZT32

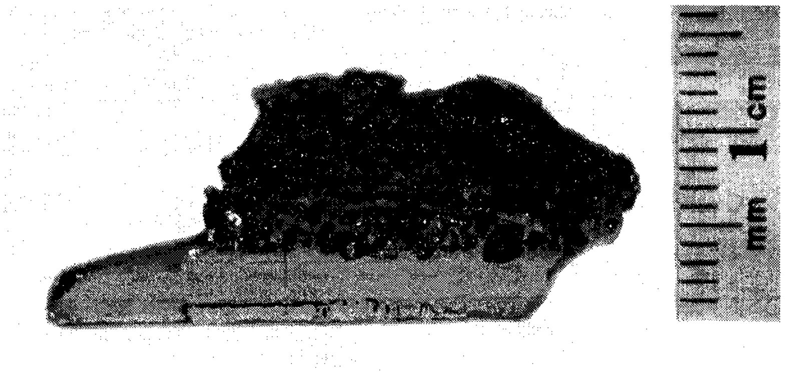


(c) CZT39 (d) CZT40

Figure 3.20: The photos above illustrate experiments where growth was initiated on only one section of the solution–substrate interface. The areas where electrical contact was ideal material has been deposited. Areas out of electrical contact have dissolved.

While island growth is far from ideal, it shows that the growth mechanisms of LPEE are working with CdZnTe. A reliable contact zone may be all that is necessary to make this a truly viable growth technique for CdZnTe. In a few experiments, very promising growth was observed. These were experiments involving thick substrates, which seemed to help with the contact problems. LPEE growth was initiated across the entire interface. In the most successful, almost $2mm$ of growth can be observed. This experiment was conducted during the solution investigations, and no source was used. If source material had been present, it is likely that even thicker growth would have been observed. The grown layers are shown in Figure 3.21.

(a) CZT35



(b) CZT33

Figure 3.21: The photos above illustrate experiments where growth was initiated across the entire solution–substrate interface. Approximately $2mm$ of growth is evident in these samples.

3.3.6 Characterization

The quality of material has not been assessed. As this work was undertaken as a feasibility study, material quality was not of primary concern. The primary goal was to show that material could be produced by LPEE. In addition, our most successful results came with using the thick polycrystal substrates. These substrates by their polycrystalline nature will introduce significant defect structure. The island growth materials, which comprised the majority of samples, were too small to be properly analyzed. Given the nature of the growth of the island material, significant defect structure would also be expected.

Section 4

Conclusion

The result of this study is that LPEE growth of CdZnTe was successfully initiated. The possibility of using LPEE as a bulk growth technique for CdZnTe is viable. LPEE remains an attractive alternative to current commercial techniques for the following reasons. Current commercial techniques have not been able to produce material reliably enough to see full utilization of the material in the marketplace [1, 2, 3, 4, 5, 6, 7]. The issues surrounding growth in melt techniques are related to physical characteristics of the material, zinc segregation, vapor pressure, etc. The issues of growing CdZnTe by LPEE, as shown in this study, are tied to the experimental design. The problems related to experimental design are solvable with continued research. Testing the graphite suspension contact zone with thick single crystal substrates could resolve the contact zone issues. The nature of LPEE growth avoids the material property problems that plague melt growth techniques. The main issue that arose from this study was the contact zone. This is a very important consideration for an LPEE apparatus as it is closely tied to the quality of growth. Further investigation is needed to find an ideal contact zone option. Once the contact issue is resolved, it is likely that CdZnTe will grow with the same success as GaInAs under LPEE [29].

The outlook for LPEE growth of CdZnTe is good. The material can be produced by LPEE. In addition, the LPEE growth system seems suited to growing this material with minimal apparatus cost. LPEE does not require the complex over pressure systems required by melt growth techniques.

4.1 Future Work

The first project to be undertaken, in order to move LPEE of CdZnTe towards a mature growth technique, is a solution to the contact zone issues. This is likely to be a substancial project given the number of variables involved. It is, however, absolutely vital to the success of LPEE growth.

Material sourcing should also be addressed. In particular, it was often difficult and expensive to obtain polycrystal material for the source and solution. This material could be synthesized using a simple vertical gradient freeze or travelling heater method apparatus. This would ensure a quality supply of material. With further study, these techniques could be used to generate the CdZnTe required for the source as well as the CdTe and ZnTe required for the solution material.

The final goal of the work will be to use LPEE as a bulk growth technique for CdZnTe. Using LPEE for bulk growth requires application of a static magnetic field over the growth cell. The magnetic field suppresses convection and allows growth to proceed at higher rates and to greater thicknesses. The effect of the magnetic field on the CdZnTe LPEE system is currently uninvestigated.

The LPEE experiments conducted at the University of Victoria have thus far been conducted in crucibles with a one inch or smaller growth diameter. For commercial applications, a diameter of at least two inches is required. The larger diameter of the system could pose difficulties for CdZnTe. The materials lower thermal conductivity could lead to pronounced radial thermal gradients over the larger diameter. These thermal gradients will adversely affect LPEE growth. A 2-inch diameter LPEE growth system is currently under development at the University of Victoria.

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Appendix A

Material Preparation and Cleaning

CdZnTe, CdTe, ZnTe Cleaning

1. Material is ultrasonically washed in acetone.
2. Material is ultrasonically washed in methanol.
3. Material is emersed in a 5% bromine, 95% methanol solution for 20 seconds. Material is kept moving in the solution.
4. Material is rinsed in methanol for 20 seconds.
5. Process is repeated eight more times. The rinse methanol is changed after three uses.
6. After cleaning the material is emersed in methanol to await loading.

NOTE: This process is used for the substrate, source and solution materials.

GaAs Substrate Cleaning

1. Material is ultrasonically washed in acetone.
2. Material is ultrasonically washed in methanol.
3. Substrate is emersed in a 1:1:4 solution of hydrogen peroxide, water and sulphuric acid for 1 minute. Material is kept moving in the solution.
4. Material is rinsed in water.
5. Material is emersed in hydrofluoric acid for 5 minutes.
6. Material is rinsed in water.
7. After cleaning the material is emersed in methanol to await loading.

Ga Cleaning

1. Material is ultrasonically washed in acetone.
2. Material is ultrasonically washed in methanol.
3. Material is emersed in a 1:9 solution of hydrochloric acid and water for 15 minutes.
4. Material is rinsed in water.
5. After cleaning the material is emersed in methanol to await loading.

NOTE: This process is used for the Ga used in the contact zone.

Al Cleaning

1. Material is ultrasonically washed in acetone.
2. Material is ultrasonically washed in methanol.
3. Material is emersed in a 1:2 solution of phosphoric acid and water for 2 minutes.
4. Material is rinsed in water.
5. After cleaning the material is emersed in methanol to await loading.

NOTE: This process is used for the Al used in the contact zone.

Quartz Cleaning

1. Quartz parts are emersed in or filled with a 3:1 solution of hydrochloric acid and nitric acid for 12 hours or until bubbling stops.

2. Quartz is rinsed in water and then filled with or emersed in water to soak for 12 hours.
3. Parts are rinsed with water.
4. If items are not in direct contact with material, like the reaction vessel, they are rinsed with methanol and dried with compressed nitrogen.
5. If items are in contact with material, they are emersed in a 1:4 solution of hydrofluoric acid and water for 20 minutes.
6. Parts are rinsed with water.
7. Parts are emersed in methanol to await loading.

NOTE: Quartz etching is undertaken between every experiment.

Crucible Bake–Out

1. Ceramic parts are emersed in pure water.
2. Parts are then cleaned in an ultrasonic washer for 5-10min.
3. The water is changed, and process repeated.
4. Parts are then emersed in methanol.
5. Parts are again cleaned in an ultrasonic washer for 5-10min.
6. The methanol is changed, and the process repeated.
7. The parts are then removed from the methanol and inserted into a furnace open to the room environment.
8. The parts are then baked at $200°C$ for 72hrs or more.

9. Finally the parts are placed in the quartz reaction tube and baked inside the LPEE system at 800°C for 24hrs or more.

NOTE: This process is only undertaken every 6 to 8 experiments.

Appendix B
Material Data

Crucible Materials

Boron Nitride

Manufacturer:	Saint Gobain
Grade:	Combat HP
Service Temp:	1150°C (Inert Environment)
Density:	$1.90 gcm^{-3}$
Thermal Conductivity:	$27.0 Wm^{-1}K^{-1}$

Pyrolytic Boron Nitride

Manufacturer:	General Electric
Grade:	Boralloy
Density:	$2.22 gcm^{-3}$
Porosity:	Non-porous

Graphite

Manufacturer:	Poco Graphite
Grade:	DFP-2 and DFP-3
Particle Size:	$4\mu m$
Density:	$1.77gcm^{-3}$
Thermal Conductivity:	$95Wm^{-1}K^{-1}$

NOTE: DFP-2 is a purified graphite, impurities less than 5ppm. DFP-3 is a densified graphite, open porosity reduced by 80%.

Molybdenum

Manufacturer:	Kamis Inc.
Purity:	99.99%

Quartz

Manufacturer:	General Electric
Purity:	99.995%

Experimental Materials

Hydrogen and Nitrogen

Nitrogen: Pre-Purified Grade, 99.99% Pure
Hydrogen: Ultra High Purity Grade, 99.999% Pure

CdZnTe

Manufacturer: Keystone Crystal
Substrate: Single Crystal, 4% Zn,
27mm x 27mm x 1.27mm
Poly Crystal, 4% Zn,
27mm x 27mm x 2.5mm
Source: Poly Crystal, 4% Zn,
27mm x 27mm x 5mm, 0.25" hole in center

GaAs

Manufacturer: Crystalloid Inc.
Substrate: Single Crystal, Mechanical Quality,
27mm x 27mm x 0.5mm

CdTe, ZnTe, Cd, Zn, Te

Manufacturer: 5N Plus
CdTe HPO Grade, 99.999% Pure
ZnTe HPO Grade, 99.999% Pure
Te HPO Grade, 99.999% Pure
Te UPN Grade, 99.9999% Pure
Cd UPN Grade, 99.9999% Pure
Zn UPN Grade, 99.9999% Pure

Ga, Al, Pt, Ta, In

Manufacturer: Sigma-Aldrich
Ga Shot, 99.9999% Pure
Al Shot, 99.99% Pure
In Shot, 99.99% Pure

Manufacturer: Alfa Aesar
Al Wire, 99.9999% Pure
Al Foil, 99.999% Pure

Manufacturer: Goodfellow
Ta Foil, 99.99% Pure
Pt Foil, 99.99% Pure

Chemicals

Chemical	**Grade**	**Assay**
Acetone	ACS Reagent	99.5% min.
Bromine	ACS Reagent	99.5% min.
Hydrochloric Acid	ACS Reagent	36.8-38%
Hydrofluoric Acid	ACS Reagent	48-51%
Hydrogen Peroxide	ACS Reagent	29-32%
Methanol	HPLC	99.8% min., 0.05% H_2O max.
Nitric Acid	ACS Reagent	68-70%
Phosphoric Acid	ACS Reagent	85% min.
Sulphuric Acid	ACS Reagent	95-98% min.

Appendix C
Equipment Data

Furnace Controller

Manufacturer:	Mellen Company
Furnace:	TT12-2.5X12M-3Z
	3 Zones, 3"–6"–3"
	12" length, 2.5" diameter
	$1200°C$ Service Temp.
Controller:	3 of Honeywell UDC 3300
	Middle zone master, end zones slaves
	1 of Honeywell UDC 100L
	Over-Temp. Alarm/Control

DC Current Source

Manufacturer:	Xantrex
Model:	XKW8-125
Max. Current	$125A$
Max. Voltage	$8V$

Vacuum System

Manufacturer:	Leybold
Rough Pump:	D2.5E Rotary Vane Pump
	Ultimate pressure, $< 1.5 \times 10^{-3} Torr$

Turbo Pump	TMP50 Turbomolecular Pump Ultimate pressure, $< 6 \times 10^{-9} Torr$