GROWTH AND MODELING OF III-V COMPOUND SEMICONDUCTOR OPTOELECTRONIC MATERIALS WITH DEVICE APPLICATIONS

By

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Several topics have been undertaken during the course of this degree which are associated with understanding and improving semiconductor processing. The growth, modeling and characterization of III-V compound semiconductor materials and optoelectronic devices has been emphasized. Epitaxial layers of $Ga_xIn_{1-x}As_yP_{1-y}$ with lattice-matched alloy compositions over the range from $x=0$, $y=0$ (InP) to $x=0.47$, $y=1$ (Ga$_{47}$In$_{53}$As) have been grown by metal organic chemical vapor deposition (MOCVD) on InP substrates. Both the MOCVD system, used to grow these layers, and a low temperature Hall effect system, used to characterize these layers, were designed and installed. The results from several other analytical techniques were used to determine the optimal growth conditions for high quality epitaxial layers.
The use of diethylzinc (DEZn), bis-(methylcyclopentadienyl) magnesium (MCp₂Mg) and dimethylcadmium (DMCd) as p-type dopant sources for MOCVD InP was investigated at BNR in Ottawa, Canada. It has been experimentally observed that the carrier concentration dependence on dopant partial pressure in the MOCVD reactor is different for each of these three dopants. A novel model of the p-doping process of MOCVD InP using DEZn has been developed that incorporates an equilibrium boundary condition between the gas phase and solid phase point defects. The results of this model indicate that at high DEZn gas phase mole fractions, which results in low solid-phase electrical activity, the dominant electrically inactive point defects are interstitial zinc and zinc complexed with a phosphorous divacancy.

A novel optoelectronic device has been fabricated and modeled which contains p-n heterojunctions in an optical interference filter. Structures were grown by molecular beam epitaxy at BNR using the GaAs/AlGaAs material system and by MOCVD at the University of Florida using the InP/GaInAsP material system. Structures with peak reflectivities at 1.3 and 1.40 microns were grown and good crystalline quality were confirmed. Electrical bistability was observed in a forty-layer device which has never been reported before in a structure of this size.
CHAPTER I
INTRODUCTION

1.1 III-V Semiconductors

Since the invention of the transistor in 1948 by Shockley, Brattain, and Bardeen, there has been a revolution in the electronics industry. Up to that time the vacuum tube diode and triode were the most used electronic devices, but then the transistor device using a semiconductor crystal as its starting material was fabricated. The microchip, which is the fundamental building block of present day computers, contains a large number of tiny semiconductor transistors using typically single crystals of silicon as a starting material. Silicon has been the "workhorse" for the electronics industry primarily due to its availability in high single crystalline purity, ease of use in device fabrication, and of course its good electrical properties. But, the relatively low electron mobility and fixed indirect bandgap of silicon makes it not suitable for present-day optoelectronic device applications. As a consequence of these new demands, research into the development of semiconductors with variable electrical and optical properties has flourished.

Compound semiconductors such as GaAs, InP and others composed of elements from group IIIA (Al, Ga, In) and group VA
(P, As, Sb) columns of the periodic table have electrical and optical properties superior to those of silicon for certain modern-day device applications. III-V materials have a wide range of bandgap energies (0.18 to 2.4 eV), where the bandgap energy is defined as the energy difference between the lowest electron state in the conduction band and the highest hole state in the valence band allowed in the semiconductor. Some compound semiconductors have direct bandgaps, meaning that the conversion of photons (light) to electrons (energy) or vice versa, does not involve a third particle, such as a phonon. The direct bandgap III-V compounds also have large electron mobilities where mobility is defined (at low electric fields) as the ratio of absolute electron velocity to the magnitude of the electric field. A listing of these parameters and the lattice constants of silicon and binary III-V semiconductors is shown in Table 1[1]. As shown in this table, as much as a two order of magnitude increase in electron mobility is possible by using III-V compound semiconductors instead of silicon for electronic devices. It is also significant to note that a wide range of compound semiconductors can be formed by creating solid solutions of the individual semiconductors; hence, a wide selection of compound semiconductors exists with a wide range of electrical and optical properties.
Table 1
Properties of Silicon and III-V Binary Semiconductors at 300 K

<table>
<thead>
<tr>
<th></th>
<th>Bandgap Type</th>
<th>Bandgap Energy (eV)</th>
<th>Electron Mobility (cm²/V·s)</th>
<th>Lattice Constant (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>indirect</td>
<td>1.12</td>
<td>1350</td>
<td>5.43</td>
</tr>
<tr>
<td>InSb</td>
<td>direct</td>
<td>0.18</td>
<td>100000</td>
<td>6.48</td>
</tr>
<tr>
<td>InAs</td>
<td>direct</td>
<td>0.36</td>
<td>22600</td>
<td>6.06</td>
</tr>
<tr>
<td>GaSb</td>
<td>direct</td>
<td>0.70</td>
<td>5000</td>
<td>6.09</td>
</tr>
<tr>
<td>InP</td>
<td>direct</td>
<td>1.28</td>
<td>4000</td>
<td>5.87</td>
</tr>
<tr>
<td>GaAs</td>
<td>direct</td>
<td>1.43</td>
<td>8500</td>
<td>5.65</td>
</tr>
<tr>
<td>AlSb</td>
<td>indirect</td>
<td>1.60</td>
<td>200</td>
<td>6.14</td>
</tr>
<tr>
<td>AlAs</td>
<td>indirect</td>
<td>2.16</td>
<td>180</td>
<td>5.66</td>
</tr>
<tr>
<td>GaP</td>
<td>indirect</td>
<td>2.26</td>
<td>300</td>
<td>5.45</td>
</tr>
<tr>
<td>AlP</td>
<td>indirect</td>
<td>2.45</td>
<td>80</td>
<td>5.46</td>
</tr>
</tbody>
</table>

Source: Streetman[1].
Since III-V compound semiconductors present a wide range in values of direct bandgap energy, mobility, and lattice constant, semiconductor devices have wider ranges of application. The bandgap energy (Eg) of a semiconductor is related to the cut-off wavelength (A) by the following equation: Eg(eV) = 1.24/A (μm). The cut-off wavelength of a semiconductor is the longest wavelength to which a detector fabricated from this same semiconductor will respond. Another degree of freedom available is the ability to form completely miscible substitutional solid solutions independently on both the group III and group V sublattices. In other words, not only simple binary III-V compounds, but also III-III'-V or III-V-V' ternary and III-III'-V-V' quaternary single crystalline semiconductors such as Al\textsubscript{x}Ga\textsubscript{1-x}As, Ga\textsubscript{x}In\textsubscript{1-x}As, GaAs\textsubscript{y}P\textsubscript{1-y} and Ga\textsubscript{x}In\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} can be created. By using ternary and quaternary semiconductors, it is possible to vary the physical and electrical properties of these materials continuously between the property limits of the constituent binary compounds listed in Table 1. A plot of the lattice constant versus the bandgap energy (at 300 K) for III-V compound semiconductors is shown in Figure 1. Solid dots indicate binary compounds, solid lines connecting dots represent direct bandgap ternary solid solutions, and dashed lines connecting dots represent indirect bandgap ternary solid solutions.
Figure 1: Lattice parameter and bandgap energy of various III-V semiconductors
Basically, the entire area bounded by the solid and dashed lines is available for use in the design of new III-V compound semiconductor devices.

The cross-hatched area shown in Figure 1 is the lattice parameter-bandgap energy space of the quaternary material $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$. This material has many optoelectronic device applications due to its wide range of bandgap energy (0.36 to 2.26 eV) and possible lattice constants. Most semiconducting single crystalline ternary and quaternary materials are epitaxially grown on a substrate of nearly the same lattice constant. Hence, the two compositional degrees of freedom available with the GaInAsP system are important because presently only GaAs, GaSb, GaP, InP, InAs and InSb are available for use as substrate materials. For GaInAsP on InP, or any other heteroepitaxial materials system, a difference of lattice constant (lattice-mismatch) of greater than 0.1% between the grown film and substrate leads to, for film thicknesses greater than the critical thickness, the formation of structural defects which can degrade device performance. This problem puts strict demands on the epitaxial growth technique employed.

1.2 Epitaxial Growth Techniques

The word "epitaxy" is derived from Greek and means "arranged upon." Epitaxial films of III-V materials are usually grown or arranged upon substrates with equivalent crystalline structure and lattice constant. The two most
common substrate materials used today for III-V homoepitaxy, (i.e., growth on a crystal of the same composition), or heteroepitaxy, (i.e., growth on a crystal of different composition or crystal structure), are GaAs and InP. The substrates are cut from bulk crystals along a particular crystal orientation from two to four inch diameter boules which are sometimes created by withdrawing a seed crystal from a heated liquid melt. Epitaxial growth on these substrates is accomplished by exposing the heated surface to a flux of group IIIA metals and group VA non-metals. The flux can be supplied from a liquid, vapor, or molecular beam source. This distinction defines the three primary methods for growing epitaxial III-V films: liquid phase epitaxy (LPE), vapor phase epitaxy (VPE), (also known as chemical vapor deposition (CVD)), and molecular beam epitaxy (MBE). Each technique has its own advantages and drawbacks, which will be discussed in the following paragraphs.

LPE is a growth technique which can be used to deposit thin single crystal layers of III-V compound semiconductors from a heated liquid solution by decreasing the temperature of the substrate relative to the solution. It is a relatively simple, inexpensive, near equilibrium (reproducible) growth technique that is well understood. The growth rate can be high and a wide range of both p- and n-type dopants are available and their incorporation is controllable. LPE has been used to grow InP[2] and high quality GaInAs[3] on InP for
laser applications. However, problems such as surface defects, poor thickness and compositional uniformity, and difficulty in growing abrupt heterojunctions have made the LPE technique unsuitable for present-day device fabrication demands. For simple layer structures such as the AlGaAs solid state laser used in compact disc players, LPE is perfectly adequate.

There are three distinct VPE or CVD chemistries: chloride CVD, hydride CVD and metal organic CVD. The chloride (or sometimes referred to as halide) CVD process for GaAs growth, as an example, uses AsCl₃ and metallic Gallium as sources in an open tube system with H₂ (as a carrier gas) to transport reactants from the source zone, through a temperature gradient zone to the deposition zone. The chloride CVD process is a surface-kinetically limited process requiring careful source composition control and accurate temperature control throughout the system for reproducibility. Also, it is difficult to vary the V/III ratio and transients are long so abruptness is bad in chloride CVD. GaInAsP has been grown by the chlorine CVD method[4] but other CVD techniques are more convenient and flexible for growing ternary and quaternary III-V compounds. Hence, the chloride process is usually only used to grow high purity epitaxial GaAs.

The hydride CVD process for growth of III-V compound semiconductors differs from the chloride process by replacing column V chlorides such AsCl₃ or PCl₃ with column V hydrides
like AsH$_3$ or PH$_3$. For InP growth, HCl gas is first reacted with liquid indium metal in the source zone. The gaseous product InCl is then carried by H$_2$ to mix and react with PH$_3$ to deposit InP in the growth zone. Similar to the chloride process, accurate temperature control is required for this three-zone process which is also surface-kinetically limited in the low-temperature growth regime. The hydride process is currently widely used for light-emitting diode (LED) applications using GaAs$_{1-x}$P$_x$. It has also found application in the growth of III-V GaInAsP and GaInAs for LED's, lasers and detectors[5]. One major advantage the hydride system provides over the chloride system is the ability to vary the vapor phase V/III molar ratio by adjusting the inlet flow rates of hydrides and HCl. One drawback of both the hydride and chloride systems is that they are hot-wall systems; interaction between the gas and heated SiO$_2$ reactor wall occurs which results in unintentional silicon incorporation into grown layers. Due to its successful use, especially in LED fabrication, hydride CVD will continue to have a significant role in the growth of III-V materials.

The third type of CVD or VPE process is metal organic chemical vapor deposition (MOCVD). The MOCVD process involves an irreversible pyrolysis reaction of vapor-phase mixtures usually of group IIIA metal organic sources and group VA hydride sources. For InP, as an example, trimethylindium (TMIn) and PH$_3$ diluted in H$_2$ would flow into an open cold-wall
quartz tube, decompose in the presence of a heated substrate, and then deposit an epitaxial layer. Under normal deposition conditions, the MOCVD process is kinetically limited by mass transport of the column III source through a stagnant layer near the growing surface. The MOCVD process is capable of growing a wide variety of films with excellent abruptness uniformity over large substrate areas. The principal device area where MOCVD has made an impact is optoelectronics. A thorough review of the MOCVD literature has been written by Ludowise[6] and a brief history of MOCVD with emphasis on InP based materials and device applications is presented in section 2.1.

Molecular beam epitaxy (MBE) is a technique capable of growing epitaxial films one atomic layer at a time. MBE makes use of controlled evaporation from one or more thermal sources to direct beams of atoms or molecules onto a heated substrate under ultra-high vacuum conditions. During a MBE growth the substrate temperature is generally kept relatively low (500-600°C for GaAs). MBE growth rates are typically slow (0.1 - 2μm/hr) which in combination with low growth temperatures permits precise layer thickness, doping and compositional control[7]. For GaAs, the As₄ beam flux is much greater than the Ga beam flux, and both fluxes are dependent upon the temperature of the effusion oven, molecular weight of the emitted atom, orifice area, and source cell to wafer distance. With a properly placed two-inch rotating wafer, nonuniformity
of the growth film may be reduced to less than ten percent. Numerous devices such as LEDs, lasers, FETs and HBTs have been fabricated with MBE. One unique bonus with MBE is that in-situ monitoring devices such as RHEED, mass spectrometers, Auger spectrometers and ion gauges are feasible and commonplace. However, large expense and limited throughput restrict MBE usage.

During the last decade, several novel deposition techniques for III-V compound semiconductors have emerged. Each one is a spin-off of either MOCVD, MBE, or a combination of the two and has some relative advantages and disadvantages; none of these new techniques are widely used. One such technique is called atomic layer epitaxy or ALE. For III-V compound semiconductors, ALE proceeds by depositing a monolayer of a group III metal followed by depositing a monolayer of group V atoms, in a layer-by-layer sequence[8]. In ALE, grown layer thickness is determined by the number of cycles rather than the time of growth. Another relatively new technique is called chemical beam epitaxy (CBE) or metal organic molecular beam epitaxy (MOMBE). In MOMBE, all of the group IIIA and VA sources are metal organic; TMAs replaces As$_4$ and AsH$_3$, TEP replaces P$_2$ and PH$_3$[9]. The remaining aspects of MOMBE are essentially the same as conventional MBE. A final technique which is similar to ALE but is performed in a conventional low pressure MOCVD system is called flow modulation epitaxy or FME. FME has been used to grow InP at
temperatures as low as 330°C by alternately pulsing PH₃ and TMIn with intervening H₂ purge steps into the reactor with each step lasting on the order of several seconds[10]. So, it is evident that there are a wide variety of epitaxial growth techniques for III-V compound semiconductors. Most of the experimental work presented in this dissertation made use of a low pressure MOCVD system. One study made use of a MBE system for a GaAs/AlGaAs device, but the rest of the literature review will focus on the use of MOCVD for growth of GaInAsP/InP materials for optoelectronic device applications.
CHAPTER II
METAL ORGANIC CHEMICAL VAPOR DEPOSITION

2.1 A Brief History of MOCVD

MOCVD refers to the deposition of multiconstituent films using one or more metal organic compounds as sources, and the term was originated by Manasevit[11]. He demonstrated that single crystalline GaAs could be deposited using TEGa and AsH₃ in an open tube reactor. Shortly after this report, it was discovered that by mixing metal organics and hydrides of different elements, binary and ternary III-V compounds such as GaP, GaAsP, GaAsSb, AlN, GaN, InAs, GaInAs, InAsP, and InP could be formed in a manner similar to GaAs[12-16]. Practical information was also reported in these early efforts such as the observation that GaAs film growth rate was mass transport limited by the metal organic group III source and independent of temperature below 800°C. Also, n-type doping using H₂S, H₂Se and p-type doping using DEZn and DMCd were achieved. Soon after the demonstration of high quality MOCVD grown material, all MOCVD grown devices such as FETs, photocathodes[17,18] and GaAs/AlGaAs DH laser diodes[19] were reported. These milestones resulted in a rapid increase in MOCVD research and development, and as a result, it has been demonstrated that MOCVD has the capability of growing a wide
variety of device quality III-V compound semiconducting materials.

The MOCVD process has been used for the epitaxy of most III-V compound semiconductors. The basic overall reaction is $M_{III}(Alk)_3(g) + X_vH_3(g) \rightarrow M_{III}X_v(s) + 2$ Alkane(g). In this reaction, the organometallic and the hydride typically are irreversibly pyrolyzed by the heat of the susceptor and substrate to form molecular (or atomic) intermediates which may react in the gas phase or on the substrate surface[20]. Some researchers say that the breaking of metal-carbon bonds occur on the semiconductor surface[21]. Contradicting reports such as these may be related to differences in test conditions or configurations from team-to-team, but the only conclusion that can be made is that the complete MOCVD process is not well understood at this time.

Each step of the MOCVD process is not known, but there are several practical trends that are generally agreed upon. Some trends for GaAs and InP are: (1) III-V MOCVD growth between 550 and 750°C is mass transport limited in the column III source (below 550°C growth is reaction limited); hence growth rates are determined by metal organic fluxes and are temperature independent; (2) for ternary and quaternary films, group III solid phase compositions are linearly related to gas phase group III compositions, however, solid phase group V compositions have a non-linear dependence on gas phase group V compositions due to large differences in cracking
temperatures (PH$_3$ is more difficult to decompose than AsH$_3$); (3) gas phase V/III ratios have a strong effect on background carrier concentrations and p- and n-type doping levels; (4) in some cases, group III metal organics react with group V hydrides to form adducts and polymers that may be involatile liquids or solids; and (5) group II alkyls act as p-type dopant sources, group VI hydrides act as n-type dopant sources, but depending on growth conditions, group IV hydrides can act as donor or acceptor sources in III-V's. The extent to which these trends apply to all III-V materials does vary, but they are definitely useful in designing an MOCVD system or in optimizing material specific growth conditions.

2.2 MOCVD Systems

Most MOCVD systems use quartz reactors oriented either vertically[11] where gas flow is usually down, or horizontally [22] where gas flow is usually over a wedge shaped susceptor. Other less common systems incorporate barrel reactors[23] where growth can occur on multiple wafers with reactants flowing from top to bottom, or "chimney" reactors[24] where gas flow is up and wafers and susceptor are held vertically. In a vertical reactor, uniform growth rates are more difficult to achieve than in a horizontal reactor because with the geometry of a vertical reactor, nonlaminar, turbulent gas flow can more easily occur. In a horizontal reactor, a boundary layer zone forms above the susceptor where the flow rate is lower than that of the bulk gas above. The stagnant layer
thickness can increase along a flat susceptor in the gas flow direction which in combination with the depletion of reactants due to deposition, can result in nonuniform grown layer thicknesses. This variation can be nullified by either tilting the susceptor at an angle of 5 to 10° or inserting a baffle into the reactor at an angle positioned above the horizontal susceptor. This gradually reduces the cross-sectional area in the reactor above the wafer resulting in a gradual increase in linear gas velocity causing the boundary layer to have a uniform thickness profile. With a constant boundary layer thickness and constant diffusion coefficient of group III source molecule, the flux of the mass transfer limited reactant to the growing surface will be constant. As a result of this, uniform semiconductor films can be grown over large area substrates.

When MOCVD growth of mixed crystals involves the use of more than one group III compound, GaInAs for example, solid phase compositional non-uniformity can result. This can result from concentration gradients in the gas flow direction due to slight differences in the magnitude of the diffusion coefficients. One way to avoid this problem is by selecting group III metal organic sources with similar molecular weights and correspondingly similar diffusion coefficients. Another way of avoiding this problem is by using low pressure (≈ 0.1 atm) operation instead of atmospheric pressure. At reduced pressures, the linear gas velocity increases and accordingly
the stagnant layer thickness decreases. Also, at lower pressures, diffusion coefficients increase, making more abrupt heterojunctions possible. Low pressure operation also reduces the occurrence probability of unwanted parasitic reactions. Because of all of these advantages, low pressure MOCVD growth has become widely used especially for multi-wafer scale-up production applications.

Another problem with the traditional horizontal "Bass type"[17] reactor is due to the fact that having a cold dense gas above a hot, less dense gas is unstable because of gravity. This can cause natural convection which results in closed stream-line gas flow patterns. This problem can usually be minimized by operating at reduced pressures[25]. The best solution, however, appears to be the use of an inverted reactor geometry[26] which completely eliminates thermal buoyancy effects. In this geometry, the susceptor is located at the highest and hottest point of a horizontal reactor with the wafer mounted upon it facing downwards. Another obvious benefit with this design is the elimination of the problem of particles falling on the substrate before and during epitaxial growth which can lead to structural defects. With this design, improved GaInAs compositional uniformity and a complete elimination of parasitic deposition on the quartz wall opposite the susceptor have also been reported[26]. Another final technique that has been used to improve both thickness and compositional uniformity is the use of moving
substrate holders in both circular and even planetary motion configurations[27]. These techniques can greatly improve uniformity, but also, unfortunately, greatly add to machine complexity and expense.

Aside from the reactor, the other major parts of an MOCVD system are the gas delivery, heating exhaust/scrubbing and safety systems. Most gas handling systems are constructed from high purity stainless steel tubing, valves (air-operated and manual), regulators, electronic mass flow controllers and filters or purifiers. The system typically delivers metal organics (from bubblers), hydrides (from high pressure gas cylinders) and most often hydrogen (from a palladium-alloy purifier) to a fast switching manifold which directs gases to the reactor or to a vent line. Gas manifolds should be situated as close to the reactor inlet as possible to minimize tube length and improve interface abruptness capabilities. Most systems use manifolds with a linear valve arrangement, but only in a radial manifold arrangement is the length from each valve to the reactor potentially the same for all of the gases[28]. In the "vent/run" type system discussed above, the vent line and reactor line are "pressure balanced" so that transient times associated with gases adjusting to and flowing from a high pressure to a low pressure line, or vice versa, can be eliminated.

For heating systems, most MOCVD reactors are heated by inductively coupling RF power to a graphite susceptor. This
is ideal because it is a non-contact method, it selectively heats only the graphite, and it is easy to configure by arranging a copper coil around the susceptor portion of the reactor. The RF generator size required depends on susceptor size, gas velocity, coupling efficiency, and reactor wall cooling mechanism. Infrared heating from quartz-halogen lamps has also been used but, as wall deposition increases, non-uniform heating may occur. A resistance heater embedded into the graphite is another option but deposition on electrical feedthroughs complicates reactor cleaning. Most heating systems use an embedded thermocouple feedback system to control temperature. Optical pyrometers have also been used but wall deposition can result in false readings.

After passing through the heated zone of the MOCVD reactor, some of the toxic gas sources still remain uncracked and undeposited. These gases have to be neutralized before being discharged into the atmosphere. Hazardous gases such as \( \text{AsH}_3 \), \( \text{PH}_3 \) and \( \text{SiH}_4 \) are commonly used in the MOCVD of III-V semiconductors and are difficult to neutralize or "scrub" especially when they are used in combination. There are four different types of scrubbing systems commercially available; depending on the application one alone may be inadequate. The four types are liquid scrubbers, thermal crackers, dry powder scrubbers, and incinerators. Liquid based scrubbers are most commonly used and work by bubbling the toxic gas through a basic (\( \text{pH} > 10 \)) solution of sodium hypochlorite and sodium...
hydroxide diluted in water where neutralized salts and acids are products. Some gases are nearly insoluble in water, though. Thermal crackers basically operate by heating the exhaust stream to approximately 950°C to thermally decompose toxic gases into less toxic compounds. Clogging and also insufficient heat transfer at high flow rates are problems with this technique. Dry scrubbers use powders such as activated carbon or diatomaceous earth mixed with iron chlorides to react with the toxic gases. This technique also has problems associated with efficient gas solid contacting and disposal of toxic corrosive powders. A final technique, the incinerator or "burn box," operates in such a way that gases are mixed with a fuel gas and oxygen and then ignited by a pilot flame or electric igniter[29]. All of the four scrubbing techniques have their individual problems. The scrubbing system should ideally be a combination of two or more of the individual systems in case one system fails.

As discussed, MOCVD of III-V compound semiconductors presently involves the use of highly toxic and explosive source gases. There has been some work on the use of less toxic sources for MOCVD such as tertiarybutylphosphine (TBP) [30] instead of phosphine (PH₃), (the threshold limit value (TLV) of PH₃ is 0.3ppm while that of TBP is greater than 1000ppm), but the material grown with these new sources is generally inferior. In any event, there must always be an integrated safety component to all MOCVD systems.
Several papers have been published on the important topic of MOCVD safety[31,32]. These papers are very useful when designing the layout of an MOCVD machine and laboratory. First, all MOCVD systems must have both toxic gas and hydrogen sensors in and around them connected to an alarm. These sensors must be capable of shutting down the machine in the event of a detected leak. In order to shut down quickly, all gas lines must be equipped with normally closed air-operated valves. Toxic gas lines should also be double contained (which is extremely expensive) and equipped with pressure sensors that sound an alarm for abnormally high pressures. Compressed air, hydrogen and nitrogen lines should have sensors for abnormally low pressure which can, if activated, shut the machine down. The reactor and pump exhaust line should also have similar pressure sensors. Of course, smoke, fire, and cooling water flow detectors and sensors are necessary. Other things such as micro-switches on panel doors and available supplied air masks are also required. Finally, SCBAs and trained users should always be available outside of the facility for emergencies. All of the above mentioned safety issues/design features are important for the design and operation of a modern MOCVD system. Of course, the most important thing for lab safety is to provide adequate operator training focusing on the nature of the toxic sources and how to treat them.
2.3 A Review of the Literature on InP Based MOCVD

2.3.1 InP Homoepitaxy

The first reported growth of indium phosphide (InP) by MOCVD was in 1969 by Manasevit and Simpson[12]. This work as well as other early efforts[33-35] used triethyl indium (TEI) and phosphine (PH₃) as indium and phosphorus sources. For several years, problems such as low, nonuniform growth rates and high impurity levels were encountered. One source of these problems was found by relating the observation of a white smoke at certain growth conditions to the uncontrolled gas phase reaction between metal organic indium sources and phosphine. This reaction occurs at low temperatures <100°C, is parasitic in nature, and produces a non-volatile liquid polymer.

One method used to minimize this problem was the use of low pressure reactor systems[36-38] to decrease the residence time of unreacted species upstream of the growth region. Another method involves the use of adducts such as TMI-TMP [39] or TMIn-TEP[40] as indium sources which will not complex with PH₃. Another technique is to keep the reactants apart and only let them mix just prior to the growth region. This method can, however, lead to uniformity problems. The most recent improvement is the use of TMIn (a solid powder at room temperature which melts at 88°C) instead of TEIn (a liquid at room temperature), as the indium source[41-43]. TMIn also decomposes at a much higher temperature (>300°C) than TEIn.
(<100°C) and therefore is less likely to react upstream of the heated growth zone. Also, TMIn has a much higher vapor pressure than TEIn which is experimentally convenient because heated gas lines would no longer be necessary.

Other techniques such as the use of hydrogen-nitrogen mixtures as the carrier gas[41] and phosphine pre-crackers[44] have been tried with varying degrees of success and merit. A final conclusion is that proper reactor geometry, system design, and growth conditions are very important for avoiding parasitic gas phase reactions and obtaining superior InP thin film quality. Currently, the reaction at certain growth conditions of TMIn and PH₃ in a properly designed MOCVD system can yield uniform, high quality epitaxial InP with no evidence of indium prereaction problems.

The deposition of high quality layers of InP for device applications requires precise control of their unintentionally introduced (undoped) and intentionally introduced (both p- and n-type doped) impurity concentrations. An important condition for obtaining reproducible p- and n-type doping levels is the ability to grow undoped material with a reproducibly low background carrier concentration. To obtain low background levels, one needs a contamination free MOCVD system equipped with high purity sources and optimized growth conditions.

Most conventional MOCVD systems are constructed from ultra-high purity components such as electropolished welded 316 stainless steel and semiconductor-grade low-sodium content
quartzware. Coupled with the use of palladium-alloy diffused hydrogen as a carrier gas, these precautions usually eliminate the system as a source of high background impurity level problems. In addition to high purity equipment, ultra high purity sources contained in stainless steel bubblers and corrosion resistant coated cylinders are required. For InP, phosphine with five nines purity (99.999%) and diphos purified (doubly sublimed) trimethylindium are both commercially available. As purification technologies advance, then progressively lower background doping levels surely will follow.

The most important material's issues in the InP growth area are the effect of growth conditions, substrate quality, substrate orientation and substrate wafer cleaning techniques on material quality. Several papers have been published on each topic and the basis of comparison presented usually involves characterization results of thin films such as room temperature (300 K) and/or liquid nitrogen temperature (77 K) mobilities and undoped carrier concentrations \((N_b - N_a) \text{cm}^{-3}\), etch pit densities (EPD), photoluminescence (PL) intensities and occasionally device performances.

The effect of growth conditions on properties of InP grown by MOCVD has been studied by several research teams\([45-48]\). Razeghi and Duchemin\([45]\) showed that the growth rate of InP is linearly dependent on indium metal organic reactor partial pressure and independent of the phosphine partial
pressure. They also compared the growth rate of undoped InP on (100), (111), and (115) InP oriented substrates and they reported excellent film quality on (100) 2° towards (110) and (115) 2° towards (111). Eguchi et al.[46] studied the effect of V/III (phosphine to metal organic indium) ratio on EPD and electrical properties and reported superior material at high V/III ratios (>300). This result was in agreement with Kasemset's[47] earlier work on both V/III ratio and growth temperature effects. However, a survey of the effect of growth temperature on layer quality is less conclusive. Kasemset[47] indicates that a decrease in background carrier concentration results upon increasing growth temperature, while Scott et al.[48] report the opposite trend. This discrepancy is probably due to different dominant impurities in each group's TMIn source with correspondingly different incorporation mechanisms. Most teams report high quality MOCVD InP grown at temperatures between 550°C and 675°C. Below 550°C, growth rates drop and material quality degrades. Above 700°C, background carrier concentrations increase.

Presently, high quality two inch diameter wafers of InP are commercially available as both doped (p - and n-type) and semi-insulating. Variation of results from team to team in early research efforts and even today may be due in part to the lack of reproducibility of substrate properties from batch to batch and vendor to vendor. A recent paper from Knight et al.[49] reports this problem. They observed a correlation
between leakage current of p-i-n InP based photodiodes and substrate quality. Consequently, they set up a nondestructive PL wafer-mapping system to evaluate grown film quality before investing further processing time. Non-destructive techniques such as PL mapping will remain essential unless wafer quality control improves.

Proper wafer cleaning is also very important for the growth of high-quality InP. Tuck and Baker[50] in 1973 published work on the chemical etching of (111) and (100) InP. They compared the merits and disadvantages of using the following four etching solutions: (1) 1HCL:1HNO₃; (2) concentrated HCl; (3) 0.4N Fe³⁺; and (4) 1% bromine in methanol, based on etching rate and hillock delineation. Nishitani and Kotani[51] presented the use of H₂O₂-H₂SO₄-H₂O solutions for etching (100) and (111) oriented InP. Recently, studies have been reported using sulphur to chemically passivate the surfaces of InP and GaAs[52-53]. The goal of this work is to reduce the substrate surface recombination velocity in order to improve device performance. Another interesting study compared several wafer cleaning methods using the surface science techniques ISS, ESCA and AES[54]. This report states that using a 5:1:1 mixture of H₂SO₄:H₂O₂:H₂O in combination with solvent degreasing step yields an InP surface with the least amount of absorbed carbon and oxygen relative to the other methods tested. Most crystal growth teams develop their
own technique of wafer preparation using a combination of the methods reviewed above.

Once an MOCVD system has been optimized for growing high purity InP and a proper substrate vendor, orientation and cleaning procedure have all been selected, most authors report that the source purity of both the metal organic indium and phosphine have the strongest influence on background carrier concentrations and mobilities. The initial work on InP growth [12,33-34] reported room temperature carrier concentrations of n=0.17 to 1.4 x 10^{16} cm^{-3} and 300 K and 77 K electron mobilities of 3500-4200 and 16,000-36,000 cm^{2}/volt-sec, respectively. After two decades of technological advancement in purification techniques and machine design, the highest reported 77 K mobility for undoped InP is now 305,000 cm^{2}/volt-sec with a corresponding carrier concentration of n= 5 x 10^{13} cm^{-3}[55].

Based on low temperature PL it appears the dominant residual acceptor in MOCVD InP is zinc[55]. For many years both carbon and manganese[47] have also been reported as compensating acceptors and silicon has been reported as the dominant donor[56]. The recent work of Bose et al.[55] caution against identifying PL peaks as carbon since the transverse optical phonon replicas of the free-exciton recombination occur at the same energy as carbon. For most teams, however, 300 K and 77 K mobilities of 4,700 and 80,000 cm^{2}/volt-sec, respectively, and a carrier concentration of n= 1 x 10^{14} cm^{-3} are typical for
undoped MOCVD InP. So, it is evident that device quality unintentionally doped InP can be grown by MOCVD.

Most semiconductor devices require a junction of some type in the host material where two materials with either different electrical or optical properties meet. An electrical junction can be created by post growth processing techniques such as ion-implantation or diffusion of a donor or acceptor into the host crystal. Another way is to just create the junction in-situ during the MOCVD growth by adding a small quantity of a donor or acceptor source into the inlet gas stream. High quality undoped InP is usually n-type with a background carrier concentration of \( n = 1 \times 10^{14} \) to \( 10^{15} \) cm\(^{-3}\). The carrier concentration \( n \) or \( (N_0 - N_A) \) can be increased by adding an InP donor species to the inlet gas stream of the MOCVD reactor. InP can be doped n-type by using \( \text{H}_2\text{S}[45] \), \( \text{H}_2\text{Se}[43] \) and \( \text{SiH}_4[43] \) or \( \text{Si}_2\text{H}_6[57] \) as sources. For each source, the free carrier concentration is essentially proportional to the dopant source mole fraction in the reactor inlet stream. Controllable n-type doping from \( 10^{15} \) cm\(^{-3}\) to \( 10^{20} \) cm\(^{-3}\) can be achieved without a significant decrease in material quality by using a combination of these sources for different parts of this wide incorporation range. Doping levels and diffusion rates of these dopants are affected to varying degrees by changes in growth conditions such as temperature, V/III ratio, and indium mole fraction. For \( \text{H}_2\text{S} \), the free carrier concentration in deposited InP layers
decreases when the growth temperature increases. For SiH₄, the opposite trend is observed, because the incorporation of silane is reaction limited whereas H₂S is adsorption limited. Si is amphoteric in InP, acting as an acceptor or donor, depending on site selection (adjusted by changes in the V/III ratio used during the growth). H₂S does not compensate itself in InP but the diffusion coefficient of S is greater than that of Si in InP. Depending on the device application, a suitable n-type dopant source for InP is apparently available.

InP can also be doped p-type by adding an InP acceptor species to the inlet gas stream of the reactor. The gas stream must contain enough of an acceptor species to increase the electrically active extrinsic acceptor level above the electrically active intrinsic donor level. The metal organic (MO) compounds DESn[45], DMZn[58], DMCd[59], Cp₂Mg[60] and MCp₂Mg[61] act as sources for acceptors in InP with varying degrees of success. There is not one single MO acceptor source which dopes InP p-type over a wide doping range (10¹⁵ - 10¹⁹ cm⁻³) without extended diffusion or surface morphology degradation. This is the reason that so many different sources have been investigated for InP as suitable p-doping sources. This dilemma, in combination with the observation that the electrical activation of some p-type dopants in InP is much less than unity, was a driving force for the extensive literature review and model development for p-doping of MOCVD InP in Chapter III of this dissertation. The most commonly
used p-dopant source is DEZn which can be used to dope InP over the range $p = 10^{15}-10^{18}$ cm$^{-3}$. DEZn is sufficient for most device applications, but its relatively high diffusion coefficient at typical growth temperatures, $D = 3 \times 10^{-13}$ cm$^2$/sec[58], does make it unsuitable for some device applications. For a more extensive discussion on p-doping of InP, the reader is referred to Chapter III of this dissertation.

2.3.2. GaInAs/InP

The ternary compound $Ga_xIn_{1-x}As$ can be grown lattice-matched to InP by MOCVD. Unlike the AlGaAs/GaAs material system, the GaInAs/InP system is not lattice-matched for all compositions. $Ga_{.47}In_{.53}As$ has an energy gap of 0.75 eV ($\lambda g = 1.67 \mu m$) and is the only composition which is lattice-matched to InP. This ternary film can be grown by carefully controlling the gallium to indium metal organic source composition of the gas inlet to an MOCVD reactor. This is one of the most severe heteroepitaxial growth scenarios possible as the group V sublattice must be changed from pure phosphorus to pure arsenic.

The first reported MOCVD growth of $Ga_xIn_{1-x}As$ was on a GaAs substrate[61] and hence was lattice-mismatched. The early efforts provided useful information such as compositional uniformity, merits of methyl versus ethyl MO sources, gas phase reactions and purity for later GaInAs/InP work. One conclusion that was useful for GaInAs/InP work was
the improvement in material quality observed upon using TEGa instead of TMGa as the gallium source. Another useful observation was that the solid phase composition is controlled by and almost equal to the gas phase ratio $[\text{TMIn}]/([\text{TMIn}] + [\text{TEGa}])$. Finally, the GaInAs growth rate is proportional to the sum of the metal organic gas phase concentrations.

Lattice-matched $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ grown on InP by low pressure MOCVD using TEGa and TEIn was first reported by Hirtz et al. [62] in 1980. As stated previously, the choice of group III alkyl sources used for GaInAs growth is critical. Using TMGa and TEIn results in poor surface morphology, whereas using TEGa and TEIn results in nearly featureless material over the composition range $0.4 < x < 0.6$ (Ga$_x$). This phenomena has been attributed to a TMGa-InP substrate steric hindrance to the heterogeneous decomposition of TEIn[63]. When growing on InP, the initial stage of growth of GaInAs is also complicated by the incongruent evaporation of phosphorus from the InP substrates upon heating. It has been shown that the morphological, optical and electrical properties of the GaInAs epitaxial layer depend heavily on minimizing InP substrate damage during the transition from PH$_3$ to AsH$_3$[64]. The best approach is using an InP buffer layer and then allowing the indium flow to continue while rapidly switching phosphine to the vent and TEGa and AsH$_3$ to a low pressure reactor.

As is the case for growth on GaAs substrates, the composition of GaInAs is linearly dependent on the flow rate
of TEGa for a fixed TEIn or TMIn flow. Both the composition and growth rate are independent of AsH₃ flow for fixed metal organic flow. The growth rate is independent of growth temperature (500-650°C), but the composition can be slightly affected due to slight differences in gallium and indium source cracking efficiencies. If the composition of a layer is different from the lattice-matched value, this layer is mismatched. The lattice-mismatch between layer and substrate is defined as \( \Delta a/a = (a_L - a)/a \), when \( a_L \) is the measured room temperature (strained) lattice parameter and \( a \) is the lattice parameter of the substrate. Razeghi et al.[38] have reported that the mobility of a semiconducting layer is dependent on the amount of mismatch in the layer relative to the substrate. At optimum growth conditions, a lattice-matching of \( \Delta a/a < 0.04\% \) has been achieved resulting in Hall mobilities of 12,000 (300 K), 100,000 (77 K) and 260,000 cm²/volt-sec (2 K) and background carrier concentrations of 0.7 - 1.0 \( \times 10^{15} \) cm⁻³[65]. Such high mobilities at 2 K are explained by the existence of a two-dimensional electron gas formed at the interface between undoped InP buffer and GaInAs layers and are indicative of superior material quality.

It is evident that MOCVD can be used to produce undoped Ga₄₇In₅₃As lattice-matched to InP, with very high quality electronic properties. Intentionally doped both p- and n-type Ga₄₇In₅₃As on InP is also producible. Razeghi[65] presented data on p-type doping using DEZn and n-type doping using H₂S
of GaInAs by MOCVD. Zinc doped GaInAs carrier concentrations are reported to decrease with increasing growth temperatures over the range $p = 10^{17} - 10^{18}\text{cm}^{-3}$. The opposite behavior is observed for sulphur doped GaInAs and this trend is confirmed by Logan et al.[66]; a carrier concentration of $\approx 10^{20}\text{cm}^{-3}$ is reported for a growth temperature of 525°C and at nearly identical conditions except $T_g = 625°C$, $n = 8 \times 10^{17}\text{cm}^{-3}$. Wide ranges of both p- and n-type doping are attainable for GaInAs on InP by MOCVD which is useful for device applications.

2.3.3 GaInAsP/InP

The quaternary solid solution $\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}$ is an alloy semiconductor which can be lattice-matched to InP and GaAs substrates. GaInAsP is a direct bandgap semiconductor (when lattice-matched to GaAs or InP) which can be a very efficient light emitter over the wavelength range 0.65 - 0.87μm (lattice-matched to GaAs) and 0.92 - 1.65μm (lattice-matched to InP). Very little work has been reported on quaternary growth on GaAs substrates[67,68] due to greater interest in GaInAsP alloys lattice-matched to InP substrates for optical fiber device applications. Optoelectronic devices operating at 1.3μm or 1.55μm wavelength regions have immediate commercial applications because light transmission through silica fibers exhibits low loss at 1.3μm and low dispersion at 1.55μm.

The MOCVD growth of GaInAsP alloys on InP substrates was first reported using ethyl alkyls in a low pressure
This same team later reported growth of nearly the entire quaternary composition range lattice-matched to InP and presented device test results of broad area and stripe lasers fabricated using six different quaternary compositions[69]. After these initial reports, numerous quaternary related papers have been published on novel growth techniques, relationship between gas phase growth conditions to solid phase compositions, electrical and optical material properties, and device applications. Each of these topics will be reviewed in the following paragraphs.

Growth techniques used for depositing quaternary alloys are direct extensions of techniques used for growing InP and GaInAs. The growth rate is similarly proportional to the sum of the partial pressure of TEGa and TMIn, and is independent of the phosphorus and/or arsenic partial pressure. Similar to the growth of GaInAs, the solid phase group III composition is essentially equal to the gas phase metal organic composition introduced to the MOCVD reactor. However, the behavior of incorporation of group V elements is different and much more difficult to control since both arsine and phosphine are required and they do not incorporate with the same probability. It is much more difficult to incorporate phosphorus than arsenic at a fixed growth temperature since the cracking temperature of PH₃ is higher than AsH₃. To alleviate this problem, some workers have used precracked PH₃[38,70] or in-situ adduct formation techniques[71] (which
is a more easily cracked species) both with varying degrees of success. Most teams use the low pressure MOCVD technique which makes \( \text{PH}_3/\text{AsH}_3 \) ratios as high as 200 (which is required for 1.0\( \mu \text{m} \) wavelength quaternaries) more safely attainable.

The operating parameters inlet partial pressures, total pressure, deposition temperature, and V/III ratio have an effect on the growth rate and composition of deposited quaternary materials. Because of this, numerous papers have been written relating the gas phase growth conditions to solid phase material quality and composition. Razeghi[65] has published graphs on which are plotted the relationship between growth conditions ratios and bandgap wavelengths for the full range of quaternary materials which are lattice-matched to InP. The three ratios are: (1) \( R_5 = \frac{\text{PH}_3}{(\text{PH}_3+\text{AsH}_3)} \); (2) \( R_3 = \frac{\text{TEGa}}{(\text{TEGa} + \text{TEIn})} \); and (3) \( R_5/R_3 \). Using these graphs, which are only valid for a growth temperature of 650°C and total flow rate of 7 liters/min, one can estimate growth conditions for any lattice-matched quaternary composition. Similarly, Fujii et al.[72] and Sugou et al.[70] present quaternary compositions as a function of (In/Ga) and (P/As) ratios in the gas phase for fixed V/III ratios. Koukitu and Seki[73] use a thermodynamic approach to compute the solid composition as a function of input mole ratio for several quaternary III-V alloy systems. They also compute the equilibrium partial pressures of gaseous species over GaInAsP/InP as a function of temperature, V/III ratio and
Using one of the above mentioned techniques, good estimates of optimum gas phase growth conditions for the full range of solid phase quaternary compositions can be predicted.

Several papers have been written presenting optical and electrical property data as a function of composition for Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ lattice-matched to InP. One important realization is that for lattice-matching, $y$ is related to $x$ by the following simple relation: $y = 2.16x$. This greatly facilitates presenting data as it can be plotted as a function of $y$ or $x$ under the assumption that the lattice-matching condition is realized. A paper by Nahory et al. [74] presents useful experimental lattice constant and bandgap values as a function of composition relative to lattice constant values predicted using Vegard's Law. Vegard's Law states that for a lattice-matched system, the lattice parameter of the quaternary can be deduced from those of the constituent binaries. This team also presents the empirical relation for bandgap variation ($E_g$ (eV)) with composition.

$$E_g(y) = 1.35 - 0.72y + 0.12y^2$$ (1)

Another group presented undoped electron and hole mobilities as a function of composition, $y$. For undoped GaInAsP, room temperature electron mobilities range from 4000 to 11,000 cm$^2$/volt-sec ($y = 0$ to $y = 1$) and room temperature hole mobilities range from 130 to 200 cm$^2$/volt-sec ($y = 0$ to $y = 1$) [75].

Both p- and n-type doping of GaInAsP/InP grown by MOCVD have been reported. Extensive doping studies as a function of
quaternary composition has not, however, been reported. Saxena et al. [76] present data on 1.3μm p-GaInAsP doped by DEZn over the range 10^{18}-10^{19} cm^{-3}, and n-GaInAsP doped by DETe and H₂S. Using tellurium, n-type doping from 3×10^{17} to 5×10^{19} cm^{-3} is reported and, with sulphur a lower range 5×10^{16} to 3×10^{18} cm^{-3} is reported. Meyer et al. [77] report n-doping of 1.3 and 1.55μm GaInAsP using H₂S over the range 10^{16} to 10^{19} cm^{-3}. It is evident that p- and n-doping of GaInAsP is possible over a wide range of doping levels which is significant for device applications.

2.3.4 InP Based Devices

The wide range of compounds that can be grown with large area uniformity by MOCVD make it suitable for fabrication of long wavelength opto-electronic device structures. Several different types of electronic, optical and opto-electronic devices have been grown by MOCVD in the GaₓIn₁₋ₓAs₀ᵧP₁₋ᵧ on InP material systems. Manasevit et al. [35] in 1978 showed that solar cells in which an InP active region grown by MOCVD can perform as well as ones fabricated by other techniques. Other devices such as lasers, field effect transistors, photo detectors and waveguides have been grown by MOCVD and will be discussed in the following paragraphs.

Some of the first devices grown using MOCVD GaInAsP were broad area and stripe double heterostructure (DH) lasers which lased at wavelengths between 1.15 and 1.54μm[69]. Distributed feedback (DFB) lasers have also been successfully grown by
MOCVD. With MOCVD, it is possible to overgrow onto sub-micron diffraction gratings which is vital to the operation of these devices[79]. A typical laser structure composed of these materials would start with a n'-InP substrate, followed by a 2μm thick n' - InP layer, then a 0.2μm active layer of lattice-matched GaInAsP (undoped), then a 2μm thick p-InP layer ending with a p' - InP contact layer of 0.2μm thickness. The lasing wavelength is determined by the composition of the active layer. Surface emitting semiconductor diode lasers, which emit light perpendicular to the grown layer surface have also been fabricated in an array form using MOCVD grown GaInAsP[80].

Microwave devices such as Gunn diodes and metal to semiconductor field-effect transistors (MESFET's) have been grown using MOCVD InP. For Gunn effect devices, even though the mobility of InP is lower than GaAs, other characteristics such as cut-off frequency, acceleration-deceleration time, relaxation time and peak-to-valley ratio are better in InP. These devices require a three-layer structure of n'-n-n'-InP grown on n'-InP and have been successfully grown by MOCVD for 60 GHz[36], and 94 GHz[81] operation. MESFET's have also successfully been fabricated by the use of undoped InP grown by MOCVD on Fe-doped substrates. The electrical properties of Au-InP Schottky diodes are reasonable and comparable to other crystal growth techniques[82].
The use of the ternary material GaInAs lattice-matched to InP for long-wavelength photodetectors is well established. Traditionally, LPE and hydride VPE are used but, MOCVD grown p-i-n photodiodes have also been prepared[65]. The most important device characteristics required of detectors are low capacitance, low dark field leakage current and high quantum efficiency. To attain these goals, low background doping levels, accurate lattice-matching and an abrupt p-n junction are required and all of these are possible with MOCVD. Actually, with MOCVD the need for a post-growth zinc diffusion processing step can usually be eliminated since in-situ p-doping is possible. Several teams have reported improvements in p-i-n photodiode performance by adjusting MOCVD growth conditions[76], layer structure[65], and Schottky barrier height enhancement[83]. MOCVD grown structures with leakage currents as low as 3 pA at -10V using a 100μm device diameter have been fabricated on two inch diameter InP substrates[84].

In addition to the above structures, a number of other optoelectronic devices have been fabricated using MOCVD grown InP based materials. Two dimensional electron gas (2DEG) and multiple quantum well structures have been grown making use of the extremely high mobilities, (in excess of 180,000cm²/volt-sec at 9.2 K) possible with these materials[85]. Guided wave devices such as optical waveguides and phase modulators have also been grown[86]. Finally, GaInAsP/InP interference filters have recently been grown by MOCVD[87]. The theory
and results of low pressure MOCVD grown GaInAsP/InP and MBE grown AlGaAs/GaAs electrically tuneable interference filters are presented in Chapter IV of this dissertation. More extensive reviews of the wide range of MOCVD grown opto-electronic devices using InP based materials are available in the literature[65,88].

2.4. **A Description of the MOCVD System**

2.4.1 **Introduction**

The experimental apparatus used for the growth of epitaxial layers of Ga_xIn_{1-x}As_yP_{1-y} on InP substrates is a commercial MOCVD system custom built for the University of Florida by Nippon Sanso K.K. (Japan Oxygen Inc.). A photograph of the front and a simplified schematic of the Japan Oxygen MOCVD System are shown in Figures 2 and 3. The complete operating procedures for performing epitaxial growths and maintenance (e.g., such as reactor cleaning), are presented in Appendix B of this text. The four basic parts of the MOCVD system which are described in the following paragraphs are: (1) the gas delivery system; (2) the reactor and heating system; (3) the exhaust/scrubbing system; and (4) the safety system. The gas delivery system, reactor, exhaust and safety system are all integrated inside the MOCVD system which is shown in the photograph in Figure 2. The heating system is a separate unit (20 kW RF generator) as is the scrubbing system which is located outside the building for ease of maintenance reasons.
Figure 2: Photograph of the quaternary MOCVD system.
Figure 3: Quaternary MOCVD simplified flow diagram.
2.4.2. Gas Delivery System

The gas delivery system connects the sources to the reactor and provides a method of transporting them in a controlled fashion. Since impurity levels must be kept to a minimum, all components of the gas delivery system are constructed from electropolished 316L stainless steel and connected with metal-gasket leak-tight couplings. Also for improved purity, 0.2μm particle filters are installed at all gas inlet points. All lines were wrapped with electrothermal heating tape and aluminum foil and are heated during standby mode to 50°C to help desorb any of the sources or impurities adsorbed on the inner walls of the stainless steel tubing.

The flow of gases is controlled by a combination of manual valves, needle valves, pneumatic valves, check valves, electronic mass flow controllers and regulators. The range of possible flow rates for each source and the carrier gases (hydrogen and nitrogen) are given in Table 2. The house nitrogen gas which is mainly used for purging the MOCVD system before a reactor or source change, passes through a molecular sieve cartridge (Matheson Model 451) before entering the machine. The house hydrogen, which is the carrier gas in the system, is purified by diffusing it through a heated (400°C) palladium-alloy membrane which is part of a 0-20 liter/min hydrogen purifier system (Matheson, Series 8370V) that was installed inside the Japan Oxygen machine.
### Table 2

Flow Rate Ranges of Sources, Vendors and Purity

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow Rate Range</th>
<th>Vendor (Purity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0-20 SLM</td>
<td>Gator Oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Alloy Diffused)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0-10 SLM</td>
<td>Linde (LN$_2$ Boil-off)</td>
</tr>
<tr>
<td>AsH$_3$</td>
<td>0-50 sccm</td>
<td>Matheson (ULSI Grade)</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>0-200 sccm</td>
<td>Solkatronic (Micropure Grade)</td>
</tr>
<tr>
<td>1000ppm H$_2$S (in H$_2$)</td>
<td>0-50 sccm</td>
<td>Matheson (ULSI Grade)</td>
</tr>
<tr>
<td>TMln</td>
<td>0-300 sccm</td>
<td>Air Products (Diphos Grade)</td>
</tr>
<tr>
<td>TEGa</td>
<td>0-100 sccm</td>
<td>Akzo (Electronic Grade)</td>
</tr>
<tr>
<td>DEZn</td>
<td>0-50 sccm</td>
<td>Morton Thiokol (Electronic Grade)</td>
</tr>
</tbody>
</table>
The gas delivery system for the metal organic sources trimethylindium, triethylgallium and p-dopant diethylzinc (which are held in stainless steel bubblers in temperature controlled baths) consists of pneumatic, needle and manual valves which are attached to the inlet and outlet ports of the bubblers. Each metal organic line also has a pressure sensor attached to it just before the inlet of the bubbler. The metal organic sources are solids or liquids at room temperature with fairly low, temperature dependent equilibrium vapor pressures. By varying the temperature of the bubbler bath, the hydrogen flow rate through the bubbler, and the pressure of the bubbler region of the gas delivery system (by opening or closing the needle valve), a controllable range of metal organic source flow rates can be attained.

Since the hydrides (arsine, phosphine) and n-type dopant (1000 ppm H₂S diluted in H₂) are highly toxic, combustible and at high pressure, the gas delivery system for these sources is slightly more complicated than for the metal organics. Each line has a regulator, air operated valve and a manifold attached to it. The manifold contains a high-pressure, high-purity nitrogen purge line, a hydrogen purge line, and a third line which can be used to evacuate the hydride line or vent the hydride source directly to the scrubber. During normal "standby" operation, palladium-alloy diffused hydrogen is purging the hydride line to the vent. Only during toxic gas flow is the hydrogen purge interrupted. Check valves on the
hydrogen and nitrogen lines prevent back flow of toxic gas through the manifold to the rest of the system.

The "heart" of the gas delivery system is the fast-switching "vent/run" manifold mounted just prior to the inlet of the reactor. The status of the "vent/run" valves (opening and closing) and the timing of this sequence can be manually or automatically controlled. Automatic control is made possible by using a process sequencer which is capable of storing 150 valve patterns and the corresponding times for each pattern or layer. The MOCVD manifold is also "pressure balanced" which means that it is possible to adjust the pressure difference between the two vent lines and the two reactor lines to almost zero. This is accomplished by carefully adjusting tube lengths and by installing a dead volume in the vent line to counter balance the volume of the reactor. Pressure balancing is especially important for MOCVD growth of superlattice or multiple quantum well structures. To keep the pressure difference between the reactor and vent lines equal to zero (which is measured using the two differential pressure indicators) each main source line has a hydrogen compensation line. It is necessary for the MOCVD growth of InP and related materials to keep the metal organics separated from the hydrides to prevent parasitic gas phase prereactions from occurring, hence the reason for the two vent/two reactor line design.
2.4.3 Reactor and Heating System

The Japan Oxygen MOCVD system has a horizontal 4 inch I.D. reactor which is equipped with a water cooling jacket (see Figure 4) to minimize side wall deposition. At the inlet of the high purity quartz reactor, two inlet lines exist to keep the group III metal organics separated from the group V hydrides at low temperatures. The dilute group III sources enter the reactor through a 6 mm O.D. high purity quartz tube 10cm downstream from the inlet of the group V sources. These two gas streams should ideally be well mixed and flowing under fully developed laminar flow conditions before the mixture encounters the high purity quartz deflector/silicon carbide coated graphite susceptor heat source. The deflector-susceptor unit is tapered at an angle of 17° with respect to horizontal to improve growth rate uniformity.

The graphite susceptor is heated by radio frequency inductive heating. A Lepel series T-15-3-KC-TL 15 kilowatt RF generator is used to generate radio waves over the frequency range 80-900 KHz. Some of these radio waves are picked up by a 3/8" copper coil that is wrapped around the reactor. A platinum/rhodium "R-type" thermocouple sealed in a high purity quartz tube is embedded inside the graphite wedge. This thermocouple is connected to a West series 2070 microprocessor based temperature controller which was installed on the MOCVD system and sends DC current to the RF generator to control
Figure 4: MOCVD reactor and loading mechanism.
its power output. Automatic temperature control from room temperature to growth temperatures (550-700°C) to bakeout temperatures (900-950°C) is possible with this elaborate heating system.

As shown in Figure 4, a high-purity quartz sample tray sits on top of part of the graphite susceptor. This tray holds substrates as large as 1/4 of a two inch diameter wafer. The tray and substrate are placed onto and removed from the susceptor by an electro-mechanical fork which is capable of precise x-y-z motion. The fork can move 90 cm horizontally from the load lock area (where the sample and tray are loaded and unloaded) through a gate valve and shutter valve, by the gas exhaust port to directly above the susceptor. Precise mechanical sample loading makes it possible to use the reactor even after side wall deposition has obstructed view of the susceptor.

To prevent the introduction of "dirty" room air to the reactor during each loading of a substrate, the air in the load-lock is evacuated by a rotary pump (Edwards model E2M2) to a roughing pressure of $10^{-2}$ torr. Then a turbomolecular pump (Balzers model TPH050) is turned on and evacuates the load-lock to a pressure of $10^{-7}$ torr. At this point the load lock is isolated and backfilled with the ultra high purity hydrogen. The sample is now ready for loading and the ultra high vacuum gate valve (VAT Ltd. model MSS4) is opened.
2.4.4 Exhaust/Scrubbing System

The waste products from the reactor flow through an exhaust port in the water cooled flange which is bolted to the exit of the reactor to a particle filter (Fuji Ltd.) which is made out of glass fibers. The gas can then either flow at atmospheric pressure directly to the scrubber or it can be evacuated from the system by a rotary pump (Edwards model E2M 18) and then continue onto the scrubber. The rotary pump makes it possible to grow films at low pressures (0.05 to 0.2 atm) which generally improves thickness uniformity.

The scrubber which was added to the Japan Oxygen MOCVD system was built by Advanced Concepts (model 9625). It is a liquid based scrubber which is designed to scrub toxic gases and exhaust clean gas to atmosphere. For safety, the exhaust was connected by a fireproof duct to the building's room air scrubber. The scrubbing solution consists of a 80:5:2 by volume mixture of water, 15% sodium hypochlorite, and 50% sodium hydroxide. The pH and oxidation reduction potential (ORP) of the scrubbing solution are constantly monitored to evaluate the solution's scrubbing potential (pH > 10.0 and ORP > 200 mV). The scrubber has an efficient gas-liquid venturi contactor and a packed bed which can handle higher than required toxic gas flow rates. For arsine and phosphine the overall chemical neutralization reactions are:

\[
\text{AsH}_3(g) + 3\text{NaOCl}(l) + \text{H}_2\text{O}(l) = \text{H}_3\text{AsO}_4(l) + 3\text{NaCl}(s) + \text{H}_2(g) \quad (2)
\]

\[
\text{PH}_3(g) + 3\text{NaOCl}(l) + \text{H}_2\text{O}(l) = \text{H}_3\text{PO}_4(l) + 3\text{NaCl}(s) + \text{H}_2(g) \quad (3)
\]
The products of these reactions are less hazardous and for added safety, when the system requires draining, the solution flows to the building's neutralization pit.

2.4.5 Safety

Arsine, phosphine and hydrogen sulfide are highly toxic combustible gases, therefore, several safety features are installed in the MOCVD system, and several safety practices must be followed in the facility. First of all, the facility has a rule that at least two competent people must be present in order to do any work in the building. The facility also has an alarm system and card reader to deny access to unauthorized personnel. The clean room has an eight point toxic gas monitor (MDA, Inc.) which has a resolution of 1 ppb for all hydrides. In the unlikely event of a toxic gas detection anywhere in the facility, the MOCVD system will completely shut down (all air-operated valves are normally closed). The MOCVD system also has a four point hydrogen gas detector (Matheson) connected to it so that if hydrogen levels exceed 50 ppm, the machine will shut down. Also the facility has a helium leak detector (Varian) which is used to find actual leak points before the MOCVD system is used and to check connections after valve replacements or reactor changes.

Not only is the facility well equipped with safety features and practices, but the Japan Oxygen MOCVD System itself has several integrated safety systems. There are two types of alarms, facility failure and machine failure. If
either power fails, compressed air pressure drops, cooling water pressure drops or temperature increases, the machine will automatically alarm and all air operated valves will close. There are smoke detectors in the machine and fire detectors in the room. There are pressure sensors on the hydride lines, in the reactor, and on the exhaust line and for each, if a certain pressure value is exceeded, an alarm will sound and the machine will shut down. There is also a pH, ORP and temperature sensor on the scrubber which triggers an alarm in the clean room if any of these values are out of the safety range. Finally, there is a compressed breathable air supply always on hand for reactor or source changes and two SCBAs available for the emergency response team. It is evident that safety is a big concern and since the machine was constructed in Japan, there is even an earthquake sensor attached to it.

2.5 Determination of Optimum Growth Conditions Based on Thin Film Characterization

2.5.1 Experimental Method

There are several experimental parameters that must be determined before performing a MOCVD growth. Using the simplest case as an example, undoped InP on InP, the first thing that must be decided is what type of substrate is required. For all of the Ga\textsubscript{x}In\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} on InP experiments performed in the Japan Oxygen MOCVD system, InP oriented (100) 2° towards (110) purchased from Sumitomo Inc. were used. Both semi-insulating (iron doped) and n-type (n ≈ 8x10\textsuperscript{18}cm\textsuperscript{-3}, sulfur
doped) InP were used together or by themselves depending on the purpose of the experiment. Next, the proper substrate cleaning procedure must be decided. Also, experimental growth conditions such as: growth temperature, growth pressure, total hydrogen flow rate, trimethylindium mole fraction, phosphine mole fraction and finally the length of time of the planned deposition, must be determined. From the literature, estimates of optimum growth conditions and proper wafer cleaning procedures can be obtained, but these values or procedures are system specific and hence had to be experimentally optimized for the Japan Oxygen MOCVD system at the University of Florida.

The procedure for calculating growth conditions for undoped InP on InP by MOCVD is fairly straightforward. The growth pressure, temperature and time must be chosen based on knowledge of the material and capabilities of the system. It should be noted that for convenience, some simplifications were made in the derivation of the equations used to calculate the growth conditions. Specifically, the ideal gas law was used and it is assumed that the total flow rate to the reactor is equal to the hydrogen flow rate and the bubbler pressure was much greater than any metal organic vapor pressure. The TMIn and PH₃ flow rates are commonly expressed as TMIn mole fraction \((\text{MF}_{\text{TMIn}})\) and PH₃ mole fraction \((\text{MF}_{\text{PH₃}})\) or their ratio, the V/III ratio, which in this case is defined as:
where:

\[
\frac{V}{\text{III}} = \frac{\text{MF}_{\text{PH}_3}}{\text{MF}_{\text{TMIn}}} \quad (4)
\]

\[
\text{MF}_{\text{PH}_3} = \frac{F_{\text{PH}_3}}{F_{\text{H}_2}} \quad (5)
\]

\[
\text{MF}_{\text{TMIn}} = \frac{F_{\text{H}_2,\text{TMIn}} \cdot \text{VP}_{\text{TMIn}}(T)}{F_{\text{H}_2} \cdot P_{b,\text{TMIn}}} \quad (6)
\]

and \( F_{\text{PH}_3} \) is the total pure phosphine flow rate (\( \text{cm}^3/\text{min} \)), \( F_{\text{H}_2} \) is the total hydrogen flow rate (\( \text{cm}^3/\text{min} \)), \( F_{\text{H}_2,\text{TMIn}} \) is the hydrogen flow rate through the TMIn bubbler (\( \text{cm}^3/\text{min} \)), \( \text{VP}_{\text{TMIn}}(T) \) (\( \text{mm} \text{ Hg} \)) is the bubbler temperature dependent TMIn vapor pressure (torr), and \( P_{b,\text{TMIn}} \) is total pressure at the TMIn bubbler (torr). All volumetric flow rates are measured at standard conditions (300 K and 760 torr). The temperature dependent vapor pressure equations for the metal organics installed in the MOCVD system which were supplied by their vendors (see Table 2) are shown in Table 3. It is therefore possible with the use of the above equations to determine conditions for a MOCVD experiment. Of course some initial values must be known and others can be based on literature values.
## Table 3

### Metal Organic Vapor Pressure Equations

<table>
<thead>
<tr>
<th>Source</th>
<th>Vapor Pressure Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMIn</td>
<td>$\log_{10} P(\text{mm Hg}) = 10.52 - \frac{3014}{T(\text{K})}$</td>
</tr>
<tr>
<td>TEGa</td>
<td>$\log_{10} P(\text{mm Hg}) = 8.224 - \frac{2222}{T(\text{K})}$</td>
</tr>
<tr>
<td>DEZn</td>
<td>$\log_{10} P(\text{mm Hg}) = 8.28 - \frac{2190}{T(\text{K})}$</td>
</tr>
</tbody>
</table>
2.5.2 InP

The method for determining the optimum growth conditions for undoped InP on InP, n-type InP on InP and p-type InP on InP will be discussed in the following sections. Before presenting the results of this operating parameter sensitivity and optimization study, the criteria for good epitaxial layers are: mirror-like low defect density surfaces, uniform growth rates over a large area substrate, less than \( n = 1 \times 10^{15} \text{cm}^{-3} \) background \((N_0 - N_A)\) doping levels for undoped InP with corresponding high room temperature electron mobilities \((\mu \geq 3000 \text{cm}^2/\text{volt-sec})\), experimentally convenient growth rates of 1-2\(\mu\)m/hour, and for doped layers and heterostructures, atomically abrupt junctions and interfaces, respectively. All of the above criteria have been determined by using various thin film characterization techniques available on the campus of the University of Florida.

2.5.2a Undoped InP

An extensive optimization study has been performed on the MOCVD growth of undoped InP on InP. The results of this study have been applied to aid in the determination of optimum growth conditions for n- and p-type InP, undoped, n- and p-type GaInAs, and undoped, n- and p-type GaInAsP on InP; these optima will be discussed later. The timing and sequence of events for a typical MOCVD growth are presented in the Appendix B of this text.
After a growth has been performed, the first property studied is the surface morphology of the thin film viewed under an optical microscope. The thickness of the film can also be determined by cleaving a sample and etching it for two minutes in a 6:4:50 solution (measured by weight) of potassium hydroxide, potassium ferricyanide, and deionized water to delineate the grown layer from the substrate and then viewing it under a microscope. A Nikon Optiphot microscope equipped with Nomarski phase contrasting was used to view the surface and delineated layer of the third growth in the machine, Q003. Polaroid photos of the images observed at 2000X magnification are shown in Figure 5. As shown, the surface morphology has a ripple in it and this is sometimes referred to as an "orange peel" surface. The side view photo of the sample was taken at the leading edge of the sample with respect to the gas flow direction. As shown, the layer thickness is clearly greater (1.5\(\mu\)m) near the corner compared to the center (1.0\(\mu\)m) probably due to the lower growth rate right on the corner which is at a different crystalline orientation, the (111) orientation.

Several experimental parameters have been varied in an attempt to improve the surface morphology of undoped InP grown on InP. The growth temperature was varied from 450 to 750\({}^\circ\)C and it was found that layers grown at temperatures between 575 and 700\({}^\circ\)C had better morphologies than those grown at higher or lower temperatures. At lower temperatures lack of
Figure 5: Nomarski photographs of an InP plane view surface and stained edge cross section taken at 2000X magnification.
adequate phosphine decomposition and at higher temperatures, slightly higher growth rates were the causes for inferior material quality. The total hydrogen flow rate and growth pressure were also varied but had little to no effect on surface morphology. The TMIn mole fraction was varied and at values greater than $1 \times 10^{-4}$ resulting material quality degraded probably due to increased growth rates. The V/III ratio had the most pronounced effect on layer surface morphology. This effect can be clearly seen in Figure 6 which shows two InP surfaces grown at identical conditions, except that the V/III ratio was almost tripled by increasing the phosphine flow rate to the reactor from 35 cm$^3$/min to 100 cm$^3$/min. This is in agreement with the growth temperature study which concluded that poor material results from insufficient phosphine decomposition.

Another study performed with the goal of improving the surface morphology of undoped InP on InP was varying the wafer preparation procedure employed. Substrates were prepared using five different techniques and then viewed under the microscope. The procedures for each are as follows: (1) filtered nitrogen blow off, five minutes each of warm acetone, warm propanol, warm methanol, and then filtered nitrogen blowoff; (2) procedure (1) followed by a 1 minute etch in 20% nitric acid in methanol, methanol rinse, DI rinse, five minute etch in room temperature 5:1:1 (sulfuric acid: hydrogen peroxide: DI water), DI rinse, methanol rinse, filtered
Figure 6: Nomarski photographs showing the effect of V/III ratio on InP surface morphology (top: V/III=50, bottom: V/III=141).
nitrogen blowoff; (3) procedure (2) without the nitric acid in methanol etch; (4) procedure (2) followed by a 1% bromine in methanol etch for 6 minutes, methanol rinse, filtered nitrogen blow dry; and (5) 2 minutes of surface treatment with the UV/ozone cleaning system (UVOCS Inc).

Under a microscope at 200X magnification, particles were observed on the surfaces prepared using procedures (1) and (2). Procedure (4) resulted in a wavy surface probably due to uneven bromine etching. Samples prepared using procedures (3) and (5) had the best surfaces. Fresh substrates were cleaned using procedures (3) and (5), loaded into the reactor, and undoped InP was grown on both of them at the same time. This experiment was performed several times and layers grown using procedure (3) were consistently equal to or better than layers grown using procedure (5). Procedure (3) was chosen as the optimum and the exact details of this procedure are given in Table 4.

The effect of growth conditions on the uniformity of undoped epitaxial InP on InP was also studied. The total volumetric flow rate was the only parameter that had any significant effect on layer uniformity. Layers grown using total hydrogen flow rates of 3, 5, 7 and 9 standard liters per minute (SLM), had corresponding thickness variations of +/-10, 8, 6 and 6%. The increased variation at the lower flow rates probably is associated with an increased boundary layer
Table 4
Optimum InP(100) Wafer Preparation Procedure

1. Cleave wafer and blow off with filtered N₂.
2. Degrease teflon beakers and tweezers with warm methanol.
3. Place substrates into beaker with warm acetone for 5 minutes.
4. Place in warm propanol for 5 minutes.
5. Place in warm methanol for 5 minutes.
6. Rinse in running DI water for 1 minute.
7. Etch in a 5:1:1 solution of H₂SO₄:H₂O₂:DI at RT for 5 min.
8. Rinse in running DI for 1 minute.
9. Place in room temperature methanol for 1 minute.
10. Blow off with filtered nitrogen.
11. Load into reactor on wafer tray from oven.
12. Anneal wafer at growth temperature for ten minutes with H₂ and PH₃ flowing.
thicknesses resulting in depletion of TMIn near the growing surface. This theory is confirmed by the observation that the growth rate was lower, 0.95 and 1.2\(\mu\)m/hour for 3SLM and 5SLM, than it was at higher flow rates (1.4\(\mu\)m/hour for 7SLM and 9SLM). The uniformity of undoped InP grown using a total hydrogen flow rate of 7SLM is presented in Figure 7. A total flow rate of 7SLM for hydrogen was chosen as optimum over 9SLM because with 9SLM at a fixed TMIn mole fraction almost 30% more TMIn material would be required.

The effect of several parameters on InP growth rate and interface quality was also studied. As already stated the total hydrogen flow rate has an effect on the growth rate. The growth pressure and V/III ratio appear, however, to have little to no effect. The growth temperature has a nonlinear effect on the growth rate; at 450°C the growth rate was 0.8\(\mu\)m/hour, but going from 550 to 750°C the growth rate only changed from 1.4 to 1.5\(\mu\)m/hour. This can be explained as follows: at low temperatures (below 550°C), InP growth is kinetically limited and consequently temperature dependent. At substrate temperatures above 550°C, InP growth is TMIn transport limited. This is confirmed by Figure 8 which shows the linear relationship between InP growth rate and TMIn mole fraction grown at 600°C. Some of the data for Figure 8 was taken from the SEM micrograph shown in Figure 9. Figure 9 is a scanning electron micrograph of a cross section from growth
Figure 7: MOCVD thickness uniformity study. Top: axial variation, bottom: radial variation at 12 mm from the leading edge.
Figure 8: The effect of TMIn mole fraction on InP growth rate.
Figure 9: SEM micrograph of growth Q054 at 20,000X. Light layers are InP, dark are GaInAs.
Q054 which shows InP layers grown with different $M_{F_{\text{In}}}$ for different lengths of time separated by thinner dark GaInAs marker layers. Figure 9 also shows the excellent abruptness of interfaces between two different materials grown at 600°C and 7SLM.

Another analytical technique used to evaluate material quality is an electrochemical C-V profiler. The C-V profiler (BioRad, Model PN4200) is thoroughly explained by Blood[89]. It uses a Schottky and ohmic contacts in an electrochemical cell filled with 0.1M HCl (for InP) to slowly etch away material while it measures the change in capacitance as a function of changing applied voltage. From this C-V data, the net carrier concentration can be calculated ($n = N_d - N_A$ or $p = N_A - N_d$, where $N_A$ and $N_d$ are the number of acceptors and donors per cm$^3$) and plotted as a function of depth. A C-V profile of growth Q056 which is undoped InP on n-type ($8 \times 10^{18}$cm$^{-3}$)InP is shown in Figure 10. From this figure one can get a rough estimate of 1.2$\mu$m for the layer thickness. Also, the epilayer-substrate interface abruptness can be assessed. Good uniformity of the carrier concentration throughout the layer can also be observed. Finally an average value of the background carrier concentration for undoped InP of $n=3 \times 10^{15}$cm$^{-3}$ can be obtained. It is evident that a lot of useful information can be obtained from an electrochemical C-V profile, the only drawback to this technique is that it is destructive.
Figure 10: C-V profile of growth Q056 (undoped InP on n+InP).
The effect of growth conditions on the background carrier concentration of undoped InP has also been studied. The growth pressure, total hydrogen flow rate, and TMIn mole fraction apparently have little effect on the background carrier concentration. The growth temperature and V/III ratio, however, both have a strong effect. The background carrier concentration measured by the C-V profiler with respect to growth temperature is plotted in Figure 11. At a low growth temperature, high carrier concentrations may be associated with phosphorus vacancies in the InP crystal (impurities are complexing with these vacancies). At higher temperatures, electrically active source impurities are incorporating more efficiently. It appears that based on background concentrations, the optimum growth temperature should be between 575°C and 625°C for undoped InP. The undoped InP carrier concentration is also strongly affected by the V/III ratio as shown in Figure 12. Based on this figure, high purity material can be grown with high PH₃ flow rates.

Another analytical technique which is commonly used to evaluate material quality is PL. The technique is explained well by Dean[90]. Briefly, it typically uses laser light energy incident upon a sample to stimulate the emission of photons at discreet energy levels. These discreet energy levels can be detected and related to impurities, defects, or host crystalline energy level transitions. The resolution of closely spaced transitions can be improved by reducing the
Figure 11: The effect of growth temperature, Tg, on undoped (n-type) InP background carrier concentration.
Figure 12: The effect of V/III ratio on C-V background carrier concentration in undoped (n-type) InP.

$H_2 = 7.0 \text{ slm, } P_g = 80 \text{ torr}$
$X_{\text{In}} = 1 \times 10^{-4}, \ T_g = 600^\circ \text{C}$
temperature of the sample. The PL spectra of two different InP samples grown at different V/III ratios and measured at 4.2 K are shown in Figures 13 and 14. The peaks labelled (D°,x) and (FE) are host crystalline donor to bound exciton and free exciton transitions. The other peaks maybe due to impurities such as carbon or crystalline defects like phosphorus vacancies (V_p). Based on the reduction in area under the peaks labelled (V_p), it is evident that increasing the V/III ratio or phosphine flow rate definitely has a positive effect of the material quality of undoped InP.

In addition to the C-V profiler, the Hall effect can also be used to determine electrical properties of semiconductors. A low temperature (room temperature to 7 K) Hall effect system was set up at the University of Florida by this researcher. The theory, and a manual explaining the use of the Hall effect system is given in the Appendix A of this text. Using data from the Hall effect system, an average value of the mobility, resistivity and carrier concentration can be calculated if the thickness of the measured film is known. These values are usually measured at 300 and 77 K (liquid nitrogen temperature) and sometimes plotted as a function of reciprocal temperature to 4.2 K. The liquid nitrogen temperature mobility (\(\mu_{77K}\)) is widely used as a measure of purity of undoped semiconducting films. In Figure 15, \(\mu_{77K}\) is plotted as a function of growth temperatures for undoped InP. The highest mobility for InP
Figure 13: PL spectrum of an InP sample grown with a V/III ratio of 140 measured at 4.2 K.
Figure 14: PL spectrum of an InP sample grown with a V/III ratio of 219 measured at 4.2 K.
Figure 15: The effect of growth temperature on 77 K mobility of undoped InP (bars indicate the range of data).
material from in the Japan Oxygen MOCVD was measured to be 61,800 cm²/volt-sec for a sample grown at a temperature of 600°C. There is a lot of scatter in the mobility data. The scatter may be due to the fact that different material sources with different impurity levels were used to grow these layers. Also, the reactor was not changed/baked-out after each growth. However, the average mobility values indicate that higher quality material can be grown at 600°C and this is in agreement with previously discussed characterization results.

Based on all of the observed characterization trends, apparent optimum MOCVD growth conditions for undoped InP on InP have been determined. These growth conditions are presented in Table 5 along with the room temperature and 77 K electrical properties of undoped InP grown at these conditions. These optimum conditions are significant because they are the basis for estimates of growth conditions for intentionally doped InP, unintentionally and intentionally doped GaInAs and GaInAsP, both lattice-matched to InP.

2.5.2b Growth of n-type InP Using H₂S

The Japan Oxygen MOCVD system was designed with the plan of using dilute H₂S as an n-type doping source. A cylinder containing a mixture of 1000 ppm H₂S and the balance ultra high purity hydrogen (Matheson, ULSI grade) is connected to the MOCVD system. The flow rate range measured at room temperature and 760 torr for this mixture, as shown in Table 2, is 0-50 cm³/min (sccm). Epitaxial layers of InP were grown
Table 5
Undoped InP Growth Conditions and Electrical Properties

Total $H_2$ Flow Rate $= 7$ SLM
Growth Temperature $= 600^\circ$C
TMIn Mole Fraction $= 0.7 \cdot 10^{-4}$
V/III Ratio $= 419$
Growth Pressure $= 80$ Torr

at 300 K:

$N_0 - N_A = 2 \cdot 10^{14}$ cm$^{-3}$ (lowest)
$N_0 - N_A = 2 \cdot 10^{15}$ cm$^{-3}$ (average)
$\mu_{300K} = 3461$ cm$^2$/volt-sec (highest)
$\mu_{300K} = 2800$ cm$^2$/volt-sec (average)

at 77 K:

$N_0 - N_A = 1 \cdot 10^{14}$ cm$^{-3}$ (lowest)
$N_0 - N_A = 2 \cdot 10^{15}$ cm$^{-3}$ (average)
$\mu_{77K} = 61800$ cm$^2$/volt-sec (highest)
$\mu_{77K} = 40500$ cm$^2$/volt-sec (average)
with H₂S mixture flow rates of 2 to 50 sccm, which corresponds to gas phase mole fractions of H₂S of 2.8x10⁻⁷ and 7.16x10⁻⁶, respectively. A C-V profile of a S-doped InP grown layer is shown in Figure 16. As one can see, a roughly 1.1μm thick layer of 2.5x10¹⁸cm⁻³ n-type material was deposited on a n⁺-InP substrate, and this was achieved using a H₂S mole fraction of 2.43x10⁻⁶. The "hump" in the profile in Figure 16 is a C-V profiler error which occurs at interfaces. The relationship between the measured C-V carrier concentration and H₂S mixture flow rate for several n-type samples is presented in Figure 17. As shown, a wide linear incorporation rate of sulfur in InP is possible resulting in doping levels from 5x10¹⁷ to 2.5x10¹⁹cm⁻³. The surface morphology of the grown material when viewed under the Nikon microscope at 2000x appeared unaffected by the presence of the sulfur atoms even at the highest n-type doping level. Room temperature Hall effect measurements were also performed on the sulfur doped samples. Hall carrier concentrations agreed with C-V measurements and Hall mobilities (μ₃₀₀K) ranged from 498cm²/volt-sec at the lowest doping level to 1064cm²/volt-sec at the highest level.

2.5.2c Growth of p-type InP Using DEZn

P-type conversion of MOCVD InP was achieved by mixing the metal organic source diethylzinc (DEZn) with the standard gas mixture used to grow undoped InP. In order to get a wide range of p-type doping, the temperature of the DEZn bubbler was varied from -20 to 20°C resulting in a change in the
Figure 16: C-V profile of a H$_2$S doped InP film.
Figure 17: The effect of $\text{H}_2\text{S}$ partial pressure on InP carrier concentration.
vapor pressure of DEZn in the bubbler from 1.39 torr to 14.00 torr. The hydrogen flow rate through the bubbler ranged from 5 to 50 sccm and by carefully adjusting the opening of the DEZn needle valve it was possible to keep the bubbler at a pressure of 500 torr.

Characterization of the p-type InP material included thickness and surface morphology measurements using the optical microscope, C-V profiles, Hall measurements and secondary in mass spectroscopy (SIMS). The SIMS technique, which is explained elsewhere[91], was used to determine the total atomic zinc concentration incorporated into several p-type InP layers as a function of depth. This total zinc level can be compared to the carrier concentration to determine the percentage of electrically active zinc atoms. Also, based on the depth of the atomic zinc profile, the extent of zinc diffusion can be assessed relative to the epitaxial layer thickness measurements. A C-V profile of growth Q080 which was deposited at Tg=600°C, Pg=80 torr and V/III=50.0 is shown in Figure 18. During the growth, a DEZn mole fraction of 4.06x10⁻⁵ was used which resulted in a C-V measured hole concentration of 1.6x10¹⁸cm⁻³, for the layer grown on the n⁺-InP substrate. A room temperature Hall effect measured hole concentration of 2.5x10¹⁸cm⁻³ was calculated for the layer grown on the semi-insulating substrate. The room temperature Hall mobility and resistivity for this p-type sample were 61.3cm²/volt-sec and 0.0402 ohm-cm, respectively.
Figure 18: A C-V profile of a DEZn doped InP film.
The relationship between the C-V measured hole concentration and the corresponding DEZn partial pressure used for the growth is plotted in Figure 19. As indicated, controllable p-type doping from $2 \times 10^{17} \text{cm}^{-3}$ to $3 \times 10^{18} \text{cm}^{-3}$ was realized. Hall measurements were attempted on all of the p-type layers grown on semi-insulating InP substrates, but the alloyed indium contacts were generally not ohmic in nature. Hence, only the C-V carrier concentration results from films grown on n-type substrates were used. The room temperature Hall carrier concentrations of semi-insulating samples with ohmic contacts agreed quite well with the C-V carrier concentrations on n-type substrates.

The effect of several growth conditions on the p-type doping of MOCVD InP was investigated. The following growth parameters: DEZn mole fraction, growth pressure, V/III ratio, growth temperature, and total hydrogen flow rate, were varied during individual experiments. It was later discovered that the effect of the extended diffusion of atomic zinc in InP during growth influenced the spatial variation of zinc's incorporation. Basically, any variation in incorporation that might have existed due to variations in growth conditions during the deposition, were negated by the rapid diffusion rate of zinc. For example, Figure 20 shows a C-V profile of growth Q105 during which the DEZn mole fraction was varied from 0.2 to $1.0 \times 10^{-5}$ and the C-V hole concentration of
Figure 19: The effect of DEZn partial pressure on InP hole concentration.
Figure 20: C-V profile of InP:Zn grown with different DEZn partial pressures.
$9 \times 10^{17}$ cm$^{-3}$ as shown, is essentially constant throughout the grown film. The large "dip" in the profile shown in Figure 20 is commonly observed at p-n electrical interfaces. A SIMS measurement was also performed on this sample (see Figure 21) and the atomic zinc concentration profile yielded essentially the same result. Similar results were observed when comparing the SIMS and C-V profiles of samples grown to study the effect of the other system parameters on zinc incorporation.

One interesting and useful conclusion that can be derived from the SIMS and C-V profiles of growth Q095, during which the growth pressure was varied from 38 to 760 torr, is the extent of zinc diffusion into the InP substrate. As shown in Figure 22, the grown layer thickness of this sample is about 1.4$\mu$m and the zinc doping level is unaffected by the change in growth pressure. In Figure 23, the atomic zinc level (from SIMS) is essentially constant throughout the profile, but a "spike" occurs in the zinc profile right at a depth of 1.4$\mu$m. The SIMS operators at BNR, where the data was taken, say that this "spike" is due to silicon-zinc complex which results from Si on the surface of the InP substrate wafer after cleaning and it reproducibly indicates the position of the grown layer-substrate interface. These "spikes" were observed in several of the SIMS profiles done at BNR. Based on the depth of the zinc profile in Figure 23, zinc has diffused approximately 0.5 microns into the InP substrate. Using this diffusion length,
Figure 21: Atomic zinc profile of sample Q105 measured by SIMS.
Figure 22: C-V profile of growth Q095 during which the growth pressure was varied.
Figure 23: Atomic zinc profile of sample Q095 measured by SIMS.
L = 0.5 microns, and the length of time that the sample was at
growth temperature, t = 90 minutes, a rough estimate of the
diffusion coefficient, D, of zinc in InP can be calculated
using this equation:

$$D(\text{cm}^2/\text{sec}) = \frac{L^2(\text{cm})}{t(\text{sec})} \quad (7)$$

A value of $D = 4.6 \times 10^{-13} \text{cm}^2/\text{sec}$ is calculated which agrees very
well with the range of values that were reported by Nelson and
Westbrook[58], $D = (1-6) \times 10^{-13} \text{cm}^2/\text{sec}$, for zinc in InP.

A review of the literature on the topic of p-type doping
of InP by several growth techniques, extensive data on zinc,
magnesium and cadmium p-type doping of InP by MOCVD, (which
was acquired when this investigator was a visitor at BNR) and
a theoretical model of the p-type doping process of MOCVD InP
is all presented in Chapter III of this text. The reader is
therefore referred to Chapter III for a more detailed and in-
depth discussion on p-type doping of InP.

2.5.3 Growth of GaInAs Lattice-Matched to InP

The mixed crystal Ga$_{47}$In$_{53}$As which is lattice-matched to
InP, has been grown using the Japan Oxygen MOCVD system. The
growth conditions used were similar to the optimum conditions
for InP growth. Based on the results of several different
characterization techniques, optimum growth conditions for
undoped Ga$_{47}$In$_{53}$As were determined. Whenever p- and n-doped
GaInAs was required for device applications, test layers were
grown to calibrate for the required DEZn and H$_2$S gas phase
mole fractions. The timing and sequence for a typical MOCVD growth of GaInAs on InP is presented in Appendix B of this text.

Since Ga\textsubscript{x}In\textsubscript{1-x}As has only one composition (x=0.47) which is lattice-matched to InP, precise control of both the TMIn and TEGA flow rates to the reactor is crucial. A small change in the TMIn to TEGA gas phase molar ratio is approximately equivalent to the change in deposited solid phase molar ratio. Unfortunately, small changes in the solid phase composition dramatically affect the material's quality and both electrical and optical properties. When the lattice-mismatch (Δa/a), where a is the lattice constant, is greater than approximately 0.5% and layer thickness is greater than the critical thickness of the material (≈1000 Å for GaInAs), the strain in the epitaxial layer is enough to form cracks or dislocations which can propagate throughout the grown film. Dislocations appear as a "cross-hatched" pattern and are clearly visible in the surface of a grown layer as viewed under an optical microscope. The surface morphology of GaInAs deposited on InP is directly related to the degree of mismatch in the thin film relative to the substrate.

Using X-ray diffraction (XRD), it is possible to determine the lattice constant of a deposited thin film relative to that of the substrate. With the lattice constant, one can determine the lattice-mismatch and composition, x, of a mixed crystal such as Ga\textsubscript{x}In\textsubscript{1-x}As. The XRD technique is
explained by Cullity[92]. It relies on the periodic structure of a crystal to scatter incident X-rays in such a way that some of the scattered beams will be in phase and reinforce each other to form diffracted beams. Scattered rays will be in phase if Bragg's law is satisfied:

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (8)

where:

\[ d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \]  \hspace{1cm} (9)

and \( \lambda = 1.54051\text{Å} \) (for copper Ka1), \((hkl)\) are miller indices (usually (004)), \(n\) is an integer (equal to 1 for first order reflection) and \(\theta\) is the angle of incidence of X-rays. Figure 24 shows the XRD spectra from two different Ga\(_x\)In\(_{1-x}\)As/InP growths. The plot on the left is the spectrum for growth Q015 which is lattice matched. The reason there are two peaks is because two different X-ray wavelengths close to each other (Ka1 and Ka2 from copper) were incident upon the sample. The spectrum on the right is from growth Q007 and it has a third broad peak at a lower 2\(\theta\) angle relative to the InP substrate peaks which when inserted into Bragg's law yields a lattice constant of \(a = 5.897\text{Å} \). This is the lattice constant of Ga\(_{0.40}\)In\(_{0.60}\)As (see Table 1 for the lattice constants of InAs and GaAs), which has a lattice-mismatch of \(\Delta a/a = 4.6\times10^{-3}\) or 0.46% on InP. If a GaInAs/InP sample had an X-ray spectrum
Figure 24: X-ray diffraction patterns of GaInAs samples grown on InP (left: lattice-matched, right: lattice-mismatched).
with more than two large peaks, like sample Q007, then no further characterization was performed on the sample.

For lattice-matched Ga\textsubscript{47}In\textsubscript{53}As on InP, the C-V profiler is a characterization technique which was routinely used. A C-V profile of growth Q005 is shown in Figure 25, which is an undoped GaInAs layer deposited on n\textsuperscript{*}-InP. As shown, the grown layer thickness is approximately 0.7μm and the substrate-epilayer electrical interface is extremely abrupt. The background doping level of this sample varies slightly from 2x10\textsuperscript{15} to 8x10\textsuperscript{14}cm\textsuperscript{3}, but the average is very low which is indicative of high quality material. The C-V profiler is less accurate for profiling lattice-mismatched GaInAs/InP samples and consequently was not used for some films.

Another technique that was used to investigate the purity and also optical properties of GaInAs/InP samples is low temperature (4.2 K) PL. Figure 26 shows the PL spectra for a precisely lattice-matched Ga\textsubscript{46.7}In\textsubscript{53.3}As on InP grown by MOCVD. Before PL was performed the degree of lattice-matching was determined by XRD. This was necessary as the PL technique is rather time consuming and it also requires a great deal of operator expertise. Also, the PL set-up was not always equipped to test the Ga\textsubscript{x}In\textsubscript{1-x}As on InP samples as they require a detector which responds to light over the wavelength range 0.9 to 1.7 microns. The spectra are quite valuable, though, as a lot of information can be derived from them. Based on the peak position in wavenumbers (inverse wavelength)
Figure 25: C-V profile of growth Q005 (lattice-matched n-type GaInAs on InP).
Figure 26: PL spectrum of GaInAs lattice-matched to InP measured at 4.2 K.
6533.556 cm\(^{-1}\), which corresponds to an energy of 0.81016 eV, and the changes in bandgap with respect to temperature (-2.285 \times 10^4 eV/K), the room temperature emission wavelength of this material is 1.67 \mu m; this is the emission wavelength of lattice matched Ga\(_{0.467}\)In\(_{0.533}\)As on InP. Hence, PL can be used to determine ternary material composition. Also, the full peak width at half of the peak's maximum (FWHM) of 3.47 meV is another indication that this layer is of excellent quality. Finally, the fact that no other peaks exist in the spectrum indicates that this sample has a very low impurity level.

The PL technique can also be used on lattice-mismatched samples. Figure 27 shows a PL spectrum of growth Q148 which was determined by the XRD technique to have the lattice-mismatched composition Ga\(_{0.435}\)In\(_{0.565}\)As. The PL spectrum agrees with XRD as the room temperature wavelength equivalent of 6380.88 cm\(^{-1}\) wavenumbers is 1.714 \mu m which would be indium arsenide-rich material. Unfortunately, the temperature dependence of mismatched Ga\(_x\)In\(_{1-x}\)As is unknown so an exact composition cannot be calculated. However, when comparing this spectrum with the one in Figure 26, it is clear based on the FWHM = 7.94 meV being larger and that two peaks exist instead of one perfect crystal transition, that the material from growth Q148 is certainly inferior to that of growth Q144 (Figure 26). When comparing PL and XRD, the PL technique is more accurate as it can correctly indicate that an epitaxial layer is lattice-mismatched when XRD incorrectly does not.
Figure 27: PL spectrum of a lattice mismatched GaInAs film on InP measured at 4.2 K.
The Hall effect was also used to investigate the quality of undoped GaInAs/InP samples. In this case, the room temperature mobility ($\mu_{300^\circ}$) and carrier concentration ($N_0-N_A$) were used as a basis of comparison between samples grown at different growth temperatures (600 to 700°C) and different V/III ratios (12.5 to 50). The Hall data for both studies are presented in Table 6. As shown it appears that a growth temperature of 600°C and V/III ratios between 25 and 37.5 yield better material. It should be noted, though, that at a V/III ratio of 25, the extended defect density was much higher than in layers grown using V/III ratios of 37.5 and 50.0.

Since it was evident that high quality Ga$_x$In$_{1-x}$As can be grown lattice-matched to InP, one important application of this material system was investigated: low dimensional structures involving heteroepitaxial GaInAs/InP superlattices and multiple quantum wells. A TEM (transmission electron micrograph) photo of a cross-section of alternating 1,150Å thick layers of GaInAs and InP is shown in Figure 28. This layer was grown as a test structure for an optical interference filter device requiring a layer pair thickness of $\approx$2000Å and also to test the interface abruptness capability of the MOCVD system. As shown, it appears that the abruptness is excellent and the layer pair thickness is very reproducible throughout the stack structure; both are equally important for good interference filter response. A SIMS profile (which was measured at VG Inc.) of another low-dimensional structure,
Table 6
Growth Temperature and V/III Ratio Studies on GaInAs/InP Material ($H_2 = 5$SLM, $P_g = 80$ Torr)

V/III = 50

<table>
<thead>
<tr>
<th>$T_g$=</th>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
</tr>
</thead>
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<td>4083</td>
<td>3411</td>
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<tr>
<td>$N_D - N_A$ (cm$^3$)</td>
<td>$3 \cdot 10^{15}$</td>
<td>$8 \cdot 10^{15}$</td>
<td>$1 \cdot 10^{16}$</td>
</tr>
</tbody>
</table>

$T_g = 600°C$

<table>
<thead>
<tr>
<th>V/III =</th>
<th>12.5</th>
<th>25</th>
<th>37.5</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{RT}$ (cm$^2$/volt-sec)</td>
<td>*</td>
<td>4763</td>
<td>5141</td>
<td>4083</td>
</tr>
<tr>
<td>$N_D - N_A$ (cm$^3$)</td>
<td>*</td>
<td>$4.5 \cdot 10^{15}$</td>
<td>$3.6 \cdot 10^{15}$</td>
<td>$8 \cdot 10^{15}$</td>
</tr>
</tbody>
</table>

Note: * --- Material was very poor and ohmic contacts were not possible.
Figure 28: TEM micrograph of alternating layers of InP (light) and GaInAs (dark) at 247,500X.
growth Q033, is shown in Figure 29. In this growth a multiple quantum well (MQW) structure was attempted using GaInAs wells (60 to 200 Å thick) which were grown between InP barriers (500 Å thick). From the SIMS profile, it is evident that the position where the phosphorus intensity drops does not exactly match the position where the gallium and arsenic intensities increase; the well barrier interface is not well defined. This was later corrected by growing a similar structure which made use of the pressure balancing feature of the MOCVD system (vent and reactor line pressures equal). A TEM cross section micrograph of growth Q136, which is almost the exact same structure as Q033, is shown in Figure 30. However, the well layer thicknesses attempted were much smaller and consequently a GaInAs quantum well of 13 Å was grown. This layer took 5 seconds to grow in the MOCVD system using the pressure balancing mode. As shown in Figure 30, heterostructures with interface abruptness down to what appears to be the atomic level, can be grown in the Japan Oxygen MOCVD system.

The PL technique can also be used to characterize the optical properties of low-dimensional layer structures such as Q136. When layer thicknesses as small as 13 Å exist, quantum size effects can be demonstrated. In Figure 31, a PL spectrum of sample Q136 is shown. In the figure several quantized peaks or energy level transitions exist. These peaks are labelled according to the individual GaInAs quantum wells
Figure 29: SIMS profile of a MQW sample (Q033).
Figure 30: TEM micrograph of MQW sample Q136.
Figure 31: PL spectrum of MQW sample Q136 measured at 4.2 K.
shown in Figure 30. Some of the peaks are not as sharp or well defined as the others, but clearly quantum energy level transitions have been realized by using PL on this sample. By using the Kronig-Penney theory[93], which is a simplified mathematical representation of the periodic potential function for electron motion, the following equation can be derived:

\[ E_n = \frac{n^2 \hbar^2}{8m^*L^2} \]  

(10)

where \( E_n \) is energy in eV, \( n = 1,2,3... \) quantum levels, \( \hbar = 6.624 \times 10^{-34} \text{J-sec} \) (Planck's Constant), \( m^* \) is the effective mass (.041 \( m_0 \), for electrons and 0.50 \( m_0 \), for heavy holes, \( m_0 = 9.109 \times 10^{-31} \text{Kg} \)) and \( L \) is the well thickness (Å). Using equation (10) one can find the theoretical confinement energy, \( \Delta E = E_{\text{peak}} - E_g = E_{c1} + E_{v1} = 6.1911 \times 10^{-19}/L^2 \text{ eV} \) (where \( E_{c1} \) and \( E_{v1} \) are the first energy levels of the conduction and valence bands, respectively). Of course the measured \( \Delta E \) is the difference between the position of each individual peak, \( E_{\text{peak}} \), and the bandgap, \( E_g \), of Ga\textsubscript{47}In\textsubscript{53}As at 4.2 K (0.812eV). A plot comparing the theoretical and experimentally measured confinement energies versus GaInAs well thickness for growth Q136 is plotted in Figure 32. The agreement is good for thinner wells but deviates from theory for thicker wells. In conclusion, the growth of low dimensional structures using the Japan Oxygen MOCVD system is possible and has been confirmed by TEM, SIMS and low temperature PL results.
Figure 32: The effect of well thickness on both experimental and theoretical confinement energy.
2.5.4 Growth of GaInAsP Lattice-Matched to InP

Unlike Ga$_x$In$_{1-x}$As, a continuous range of compositions exist for the mixed crystal Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ which are lattice-matched to InP. The As$_y$ composition can be varied from $y=0$ (InP) to $y=1.0$ (Ga$_{47}$In$_{53}$As), but since the relation $y=2.16x$ exists for lattice-matched quaternary, Ga$_x$ is constrained to only vary from $x=0$ (InP) to $x=.47$ (Ga$_{47}$In$_{53}$As). This wide range of variable composition corresponds to material which can emit light at wavelengths from 0.92 $\mu$m ($y=0$) to 1.65 $\mu$m ($y=1$), (see Figure 1) and several layers of lattice-matched quaternary over this wavelength range have been successfully grown in the Japan Oxygen MOCVD system.

The MOCVD growth conditions for Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ on InP were based upon the optimum growth conditions for Ga$_{47}$In$_{53}$As on InP. It has been experimentally determined that the following gas phase growth conditions and the relationship between them all have a strong influence on solid phase material quality: $\text{MF}_{\text{In}}/\text{MF}_{\text{TEGa}}$, $\text{F}_{\text{PH}}/\text{F}_{\text{ASH}}$, and the V/III ratio. The exact values of these three ratios are strongly composition dependent and initial estimates of these values for a specific solid phase composition were taken from the literature[72]. In Figure 33, the effect of growth conditions on material quality (lattice-matching) is clearly shown. The upper photo is of a sample from growth Q036 and it has the characteristics of a lattice-mismatched sample, point and line
Figure 33: Surfaces of quaternary films grown on InP (top: lattice-mismatched, bottom: lattice-matched).
dislocations. The lower photo is of a sample (Q120) that appears to be lattice-matched. The degree of mismatch can be determined more accurately by XRD, but since there are two unknowns, x and y, the exact composition of a lattice-mismatched quaternary film cannot easily be determined with this technique. The percent of lattice-mismatch (100 x Δa/a) for samples Q036 and Q120 are -0.824% and 0.00%, respectively. The degree of lattice-mismatch for both of these samples was determined from their XRD spectra which are shown in Figure 34. All that one can tell from the higher angle peak position of the quaternary material in spectrum Q036, other than the lattice constant, is that it has too much GaAs_{1-y}P_{y} to be matched.

One way of getting a "rough" idea of the composition of Ga_{x}In_{1-x}As_{y}P_{1-y}/InP films is by using the electron microprobe analysis (EPMA) technique. This analytical tool is available in the Materials Science and Engineering Department on campus, but it is not extremely accurate. It was useful, however, for calibrating the growth conditions as the technique does not require that the deposited film is lattice-matched or nearly lattice-matched to the substrate used. It gives the detected weight fraction or atomic fraction of elements which are being emitted from the electron bombarded surface. The EPMA analysis of sample Q120 yielded a quaternary composition of Ga_{0.353}In_{0.647}As_{0.80}P_{0.20}. Another technique which determines more precisely the composition of a lattice-matched quaternary film
Figure 34: X-ray diffraction patterns of quaternary films grown on InP substrates (left: lattice-matched, right: lattice-mismatched).
is PL. The PL spectrum for growth Q120 is shown in Figure 35. Based on the location of the peak position, and the temperature dependence of the quaternary bandgap, the room temperature emission wavelength of sample Q120 is $\lambda = 1.554 \mu m$. This wavelength for lattice-matched quaternary corresponds to a composition of $\text{Ga}_{4.4}\text{In}_{6.6}\text{As}_{91.3}\text{P}_{0.087}$ according to Table I of Nahory et al.[74]. A comparison of the PL and EPMA results for all lattice-matched quaternary samples are shown in Table 7. As shown, the agreement for some samples is quite good, but for others, Q242 for example, the agreement is poor. This probably is due to the fact that only InP, GaAs, and a lattice-matched GaInAs (on InP) sample were used to calibrate the EPMA detected atomic analysis results. It would have been ideal to have also used an InAs and GaP sample, but these crystals were not available for calibration. Consequently, whenever samples were found to be lattice-matched by XRD, PL was performed and solid phase compositions were based on PL peak positions. The EPMA results were, however, generally close, and they were also used as feedback for lattice-matching studies when quaternary samples were too mismatched for XRD and PL analysis.

PL can also be used to assess grown quaternary film quality based on the shape of peaks, the number of peaks and also their location in the spectrum. The FWHM of sample Q120 was measured from the spectrum to be 4.46 meV at 4.2 K.
Figure 35: PL spectrum of sample Q120 measured at 4.2 K.
Table 7
Photoluminescence and Electron Microprobe Analysis of Nearly Lattice-Matched Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ Films Grown on InP by MOCVD

<table>
<thead>
<tr>
<th>Run</th>
<th>PL</th>
<th>PL($\lambda_{RI}$)</th>
<th>EPMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q035</td>
<td>Ga$<em>{.437}$In$</em>{.563}$As$<em>{.960}$P$</em>{.040}$</td>
<td>1.605µm</td>
<td>Ga$<em>{.420}$In$</em>{.580}$As$<em>{.994}$P$</em>{.006}$</td>
</tr>
<tr>
<td>Q119</td>
<td>Ga$<em>{.330}$In$</em>{.670}$As$<em>{.761}$P$</em>{.239}$</td>
<td>1.427µm</td>
<td>Ga$<em>{.170}$In$</em>{.830}$As$<em>{.560}$P$</em>{.460}$</td>
</tr>
<tr>
<td>Q120</td>
<td>Ga$<em>{.400}$In$</em>{.600}$As$<em>{.761}$P$</em>{.239}$</td>
<td>1.554µm</td>
<td>Ga$<em>{.353}$In$</em>{.647}$As$<em>{.800}$P$</em>{.200}$</td>
</tr>
<tr>
<td>Q164</td>
<td>Ga$<em>{.390}$In$</em>{.610}$As$<em>{.895}$P$</em>{.105}$</td>
<td>1.532µm</td>
<td>Ga$<em>{.410}$In$</em>{.590}$As$<em>{.900}$P$</em>{.100}$</td>
</tr>
<tr>
<td>Q165</td>
<td>Ga$<em>{.320}$In$</em>{.680}$As$<em>{.745}$P$</em>{.255}$</td>
<td>1.400µm</td>
<td>Ga$<em>{.300}$In$</em>{.700}$As$<em>{.720}$P$</em>{.280}$</td>
</tr>
<tr>
<td>Q238</td>
<td>Ga$<em>{.346}$In$</em>{.654}$As$<em>{.787}$P$</em>{.213}$</td>
<td>1.469µm</td>
<td>Ga$<em>{.314}$In$</em>{.686}$As$<em>{.722}$P$</em>{.278}$</td>
</tr>
<tr>
<td>Q239</td>
<td>Ga$<em>{.301}$In$</em>{.699}$As$<em>{.706}$P$</em>{.294}$</td>
<td>1.371µm</td>
<td>Ga$<em>{.242}$In$</em>{.758}$As$<em>{.567}$P$</em>{.433}$</td>
</tr>
<tr>
<td>Q242</td>
<td>Ga$<em>{.283}$In$</em>{.717}$As$<em>{.629}$P$</em>{.371}$</td>
<td>1.324µm</td>
<td>Ga$<em>{.030}$In$</em>{.970}$As$<em>{.042}$P$</em>{.957}$</td>
</tr>
<tr>
<td>Q251</td>
<td>Ga$<em>{.159}$In$</em>{.841}$As$<em>{.350}$P$</em>{.650}$</td>
<td>1.115µm</td>
<td>Ga$<em>{.121}$In$</em>{.879}$As$<em>{.333}$P$</em>{.667}$</td>
</tr>
</tbody>
</table>
This, in addition to the observation that the spectrum of Q120 has no other peaks, indicates that the film's compositional uniformity throughout the film and purity of the film are both quite good. The FWHM of the PL peak for sample Q239 ($\lambda_{RT} = 1.371 \mu m$) is 15.5 meV. This spectrum is shown in Figure 36 and was taken at 13 K which partially accounts for the larger peak width due to increased lattice vibration at the higher measurement temperature. It may also be that the control of the composition during the MOCVD growth of sample Q239 was inferior to that of sample Q120.

Another way of determining the purity of quaternary films is by measuring the background carrier concentration of undoped layers with the C-V profiler. In addition, the Hall effect can be used to measure the average background carrier concentration and the mobility of the layer. A C-V profile of sample Q239 is shown in Figure 37 and from this profile an average background carrier concentration of $2 \times 10^{16} \text{cm}^{-3}$ was measured. The room temperature Hall carrier concentration and mobility of this same sample were measured to be $1.8 \times 10^{16} \text{cm}^{-3}$ and 4630 cm$^2$/volt-sec, respectively. The lowest Hall carrier concentration of an undoped quaternary film was $1.10 \times 10^{15} \text{cm}^{-3}$ for sample Q166. The highest room temperature Hall mobility measured was 4810 cm$^2$/volt-sec for sample Q037. Of course these values are composition dependent; higher mobilities are expected from compositions closer to $y=1$ (GaInAs).
Figure 36: PL spectrum of sample Q239 measured at 13 K.
Figure 37: C-V profile of a n-type quaternary film on InP.
CHAPTER III
P-TYPE DOPING OF MOCVD INP: EXPERIMENTS AND MODELING

3.1 A Review of the Literature on p-Type Doping of InP

3.1.1 Introduction

Epitaxial layers of the III-V compound semiconductors InP, GaInAs and GaInAsP with compositions lattice-matched to InP are widely used for the fabrication of optoelectronic devices. Many optoelectronic devices rely on the creation of an electrical p-n junction using p-type InP. InP doped p-type by MOCVD and other crystal growth techniques can be made, but the process is not understood in detail. At this time, an "ideal" p-type dopant with the following characteristics does not exist: (1) a wide controllable doping range \( p = 10^{15} - 10^{19} \text{cm}^{-3} \); (2) a low bulk diffusivity \( D < 10^{-15} \text{cm}^2/\text{sec} \); (3) a controllable incorporation rate for a wide range of growth conditions (growth temperatures, V/III ratios, group III concentrations); (4) full electrical activity \( p = \text{atomic concentration} \); (5) no memory effects in the system; and (6) one that does not degrade layer morphology by the formation of extended defects.

Several material sources have been used to incorporate Hg, Cd, Mg, Zn, Mn, Be, Cu, Ca and C atoms as p-type dopants in InP, with varying degrees of success[94-96]. Because of
this dilemma, an attempt has been made to understand the process of p-type doping of InP with the ultimate goal of identifying an "ideal" p-type dopant source. A review of the literature on bulk crystal growth, LPE, MBE and CVD (metal organic, chloride, and hydride) of p-type doping of InP has been performed. From this search, data on the relationship between the dopant distribution in the solid phase and the growth conditions from either the liquid or gas phase have been used to determine if the process is at equilibrium, reaction limited, or transport limited. For gas phase growth, it is evident that dopant incorporation occurs by a reaction or transport limited process. For the liquid phase growth, incorporation occurs from a near equilibrium process at the solid-liquid interface which is also transport limited in the liquid bulk.

3.2 Bulk Crystal Growth

P-type InP substrates have been used for radiation resistant solar cells[97], buried heterostructure lasers[98], and other modern optoelectronic device applications. Liquid encapsulated Czochralski (LEC) pulling is the most widely used technique for growing bulk p-InP substrates. Usually a layer of liquid B₂O₃ seals the heated InP melt and a seed crystal is dipped into the melt and slowly pulled out at a rate which controls the crystal diameter. Cd, Zn, Be, Mg and Mn have been used as p-type dopants for InP bulk crystals[99]. Zn is the most commonly used dopant due to its experimentally
convenient near unity effective distribution coefficient; $K(\text{Zn}) = 0.6^{[99]}$, $K(\text{Zn}) = 1.4^{[100]}$. Zn is a fast diffuser in InP ($D=(1-6)\times10^{-13}\text{cm}^2/\text{sec}^{[58]}$), so in situations where abrupt doping profiles are required, Cd doping is sometimes used. The distribution coefficient of Cd is low though, $K(\text{Cd}) = 0.1-0.2^{[99]}$. This means that as the crystal is pulled, the Cd concentration in the melt increases and as a result, the atomic concentration in the solid also increases. Zn doped InP bulk crystals have been fabricated by LEC and the characteristics of the material have been reported by Roksnoer and Van Rijbroek-Van Den Boom^{[101]}. They report a Zn distribution coefficient of $K(\text{Zn}) = 0.90$ which is constant over the atomic concentration range of $[\text{Zn}] = 7\times10^{17}$ to $2\times10^{19}\text{cm}^{-3}$. They also report that their material was dislocation free for concentrations greater than $[\text{Zn}] = 1\times10^{18}\text{cm}^{-3}$. The most interesting data, however, were their Hall carrier concentration results. Their observation was that for crystals containing less than $5\times10^{18}$ zinc atoms/cm$^3$, $p \approx [\text{Zn}]$ but, at $[\text{Zn}] > 5\times10^{18}\text{cm}^{-3}$, $p < [\text{Zn}]$. At the highest atomic level $[\text{Zn}] = 2.4\times10^{19}\text{cm}^{-3}$, $p = 1.5\times10^{18}\text{cm}^{-3}$. Thus, a significant part of the zinc atoms were electrically inactive. They propose that precipitates had been formed in the heavily doped crystals. But in only the most heavily doped one ($[\text{Zn}] = 2.4\times10^{19}\text{cm}^{-3}$), were small pits detected by preferential etching. It is possible that Zn at high doping levels also incorporates in some unknown form as a donor, compensating the
material and reducing the net hole concentration. Theories such as this one are proposed and considered in the model development portion (section 3.4) of this chapter.

3.1.3 Liquid Phase Epitaxy

The LPE technique has been successfully used to fabricate many optoelectronic devices which use p-InP layers as part of the device structure. Zinc[2], magnesium[2], cadmium[2] and manganese[102] have been successfully used to achieve p-type conversion in LPE grown InP and related materials. The dopants are added to the In melt in pure metallic form, or as alloys. The distribution coefficients for Zn, Cd and Mg in InP by LPE are 0.7, 0.001 and 0.05-0.5, respectively[2]. Zinc is the most commonly used dopant for several reasons. It controllably incorporates to form p-type material with hole concentrations from \( p = 1 \times 10^{16} \) to \( 2 \times 10^{18} \text{ cm}^{-3} \), whereas with Cd, p-doping levels from \( p = 5 \times 10^{16} \) to \( 2 \times 10^{18} \text{ cm}^{-3} \) exist[2]. With Mg, hole data were uncontrollably scattered from \( p = 2 \times 10^{17} \) to \( 6 \times 10^{18} \text{ cm}^{-3} \)[2]. Mn is only capable of doping material at low p-levels from \( 3 \times 10^{16} \) to \( 1 \times 10^{17} \text{ cm}^{-3} \)[102]. Cd diffuses less than Zn and much less than Mg. But, the equilibrium vapor pressure of Cd (at 625°C) is eight times greater than that of zinc (200 vs. 25 torr). Hence, Cd rapidly evaporates from the heated melt, which results in varying doping level profiles and contamination of neighboring melts. Consequently, Zn is the preferred p-type dopant for LPE growth of InP.
Wada et al. [103] also presented Zn doping results for LPE InP. They report a distribution coefficient of $K(\text{Zn}) = 0.84$ for a Zn fraction in the melt of $10^{-2}$ atomic percent which corresponds to a hole concentration of $2 \times 10^{18} \text{cm}^{-3}$. Above this Zn fraction, they report constant then decreasing Hall hole concentrations and attribute this trend to strong compensation effects. Interestingly, this is the same trend that was observed for bulk crystal growth of Zn doped InP. Wada et al. [103] suggest (without evidence) that the decrease in carrier concentration may be due in part to precipitate formation, but is more likely due to compensation by an interstitial zinc donor complex as proposed by Hooper and Tuck [104].

3.1.4 Molecular Beam Epitaxy

P-type doping of InP grown by MBE has been attempted using several different group II atoms. Zn and Cd were used as dopant atoms by Park et al. [105] emanating from a low energy ion cell during InP MBE growth. Doped films remained n-type due to the near zero sticking coefficient of these atoms on InP at the growth temperature $\approx 350^\circ \text{C}$. Be doping of MBE InP grown at 525°C has been reported by Panish et al. [106]. They report successful p-type conversion using Be with hole concentrations from $p = 6 \times 10^{16} \text{cm}^{-3}$ to $p = 1 \times 10^{19} \text{cm}^{-3}$ with corresponding Hall mobilities of $\mu_h = 100$ to 30 cm$^2$/volt-sec. Recently, Mg has been used as a potential p-type dopant for MBE InP grown at 500°C. Cheng et al. [107] reported for all layers up to the maximum beam equivalent pressure of Mg =
1x10^-9 mbar, p-type conversion was not obtained. Apparently, the Mg sticking coefficient is very low for MBE-InP unlike MBE-GaAs where Mg has been successfully applied[107]. To date, Be is the most successful p-type dopant for MBE InP.

3.1.5 Chemical Vapor Deposition

3.1.5a Hydride

The hydride CVD technique has also been used to grow p-type InP layers as part of optoelectronic device structures. In the review by Olsen[108], two different methods are mentioned for p-doping InP by the hydride technique and both involve zinc. One method uses flowing hydrogen to carry elemental zinc vapor from a heated "zinc bucket" into the mixing zone of the reaction tube. A second method mentioned uses diethylzinc as a p-type dopant source for InP, but there are no electrical results presented for either technique. A third technique is presented by Jurgensen et al.[109] which made use of a Zn doped indium source. The weight fraction of Zn in the indium was varied from 0.6 to 4.5x10^-5. The hole concentrations of several subsequently grown layers from each In/Zn mixture are presented. Surprisingly, independent of the amount of Zn added to the indium source, the experimental hole concentrations scatter around the same curve and appear to only depend on the length of time that the source was heated. Hole concentrations start at p = 1x10^{18}cm^{-3} (run #1) and increase to 2.5x10^{18}cm^{-3} (run #4). They then decrease to 9x10^{17}cm^{-3} (run #9). Perhaps as time goes on, from run to run,
zinc is being gradually depleted from the In/Zn melt due to incongruent evaporation. The first three samples may actually have a higher atomic zinc concentration than sample #4, but they are compensated due to the incorporation of interstitial donor complexes. This theory agrees with the observed trend and also with the trends seen for both bulk-grown and LPE-grown Zn-doped InP.

3.1.5b Chloride

P-type InP has also been achieved by the chloride CVD technique. Both Zn and Cd doped InP have been reported by Chevrier and co-workers[110,111]. In the Zn doped InP paper [110], 1 gram of Zn was added to the In melt which was heated to 750°C. Hole concentrations are given for consecutive samples which were grown from the same In/Zn melt. The hole concentration decreases as the number of runs increases and this trend is attributed to Zn depletion in the source[110]. SIMS measurement results of the atomic zinc concentration [Zn] are also given for a few samples, and the ratio [Zn]/p varies from 2.35 for the low doped sample ([Zn] = 2x10^{18} cm^{-3}) to 9.25 for one of the highest doped samples ([Zn] = 3.7x10^{18} cm^{-3}). The low doped (p = 8.5x10^{17} cm^{-3}) sample was annealed for two hours at 300°C and the hole concentration was again measured by the Hall effect method. It was reported to increase to p = 2x10^{18} cm^{-3}, which is the same value as the measured SIMS concentration, [Zn]. The authors propose that the annealing process activates neutral Zn atoms[110]. It is this writer's
opinion that the grown-in compensating donor zinc complexes disassemble upon annealing to create a defect structure which eventually contains only electrically active zinc acceptors.

Similar to the zinc doping paper, Chevrier et al.[111] have published a paper on Cd doping of chloride CVD InP. They report a linear incorporation of Cd with hole concentrations (deduced from Hall effect and C-V measurements) in the range $p = 1 \times 10^{15}$ to $3 \times 10^{18}\text{cm}^{-3}$. For cadmium partial pressures below $1.5 \times 10^{-4} \text{ atm}$, a distribution coefficient $K(\text{Cd}) = 0.2$, is reported. Above $p_{\text{Cd}} = 1.5 \times 10^{-4} \text{ atm}$, they report that strong compensation limits the hole concentration to a constant value of $3 \times 10^{18}\text{cm}^{-3}$ (for partial pressures up to $P_{\text{Cd}} = 8.0 \times 10^{-2} \text{ atm}$). Chevrier et al.[111] also performed annealing experiments on the Cd doped samples and found the opposite trend as reported for the Zn annealing experiments[110]; hole concentrations decrease with longer annealing times at 300°C. The cadmium trend, they propose, may be due to increased neutral complex formation, increased clustering of Cd, activation of a donor compensating complex, or deep diffusion of Cd. They also reported gradually decreasing growth rates at high (above $1.5 \times 10^{-4} \text{ atm}$) Cd partial pressures. Because of this fact, and the relatively high $p_{\text{Cd}}$ used, this writer has concluded that the clustering explanation is the most logical explanation.

3.1.4c **Metal Organic**

MOCVD has been applied to the growth of p-type InP epitaxial layers for optoelectronic device structures. To
date, Cd, Mg and Zn have been used as dopant species for p-type doping of MOCVD InP. Several different organometallic compounds have been used as Cd, Mg and Zn sources such as: dimethylcadmium (DMCd)[58,59,112], cyclopentadienyl magnesium (Cp₂Mg)[58], bis-(methylcyclopentadienyl) magnesium (MCp₂Mg) [113], diethylzinc (DEZn)[45,58,112] and dimethylzinc (DMZn) [58]. The relative merits and disadvantages of the use of each dopant will be discussed pertinent to specific desired device characteristics.

The use of Cd as a p-type dopant for MOCVD InP has been reported by several researchers[58,59,112]. Blaauw et al.[59] report atmospheric and low pressures MOCVD growth using TMIn, PH₃ and DMCd. Nelson and Westbrook[58] report atmospheric pressure MOCVD growth using adducts. The same doping trend was reported by Blaauw et al.[59] and Nelson and Westbrook [58]; a linear incorporation rate of Cd from p = 5x10¹⁵ cm⁻³ to 2x10¹⁸ cm⁻³ (measured by Hall) due to a change in DMCd partial pressure from 1x10⁻⁶ to 3x10⁻⁴ atm. Blaauw et al.[59] reported this trend for both atmosphere pressure and low pressure (76 torr) growths, but observed extended layer morphology deterioration at high DMCd partial pressures for only low pressure growths. Nelson and Westbrook[27] also investigated the effect of growth temperature (Tg = 550-650°C) on DMCd incorporation. They observed that as the growth temperature is decreased, the hole concentration at a fixed DMCd flow rate, increased. They attribute this trend to increased Cd or
DMCd desorption from the growing layer at high temperatures. They also measured the diffusion coefficient of Cd from SIMS profiles and report a value (at 600°C) of $D_{\text{Cd}} = 0.4$-$1.4 \times 10^{15}$ cm$^2$/sec. Yang et al. [112] presented data for one DMCd simultaneous InP deposition on three different orientations of InP. They reported carrier concentrations of $p = 1.1 \times 10^{17}$ cm$^{-3}$, $p = 8.7 \times 10^{17}$ cm$^{-3}$ and $n = 1 \times 10^{16}$ cm$^{-3}$ for the (100), (111A) and (111B) orientations, respectively. The Cd incorporation is most efficient on the (111A) orientation possibly due to the increased number of Indium vacancies on this type of surface. Overall Cd seems to be a fairly good p-type dopant due to its wide incorporation range and low bulk diffusivity, but it is not a suitable dopant for low pressure growth applications due to the deterioration in surface morphology.

The use of Cp$_2$Mg [58] and MCp$_2$Mg [60] as precursors for Mg p-type doping of InP has been reported. Nelson and Westbrook [58] performed atmospheric pressure adduct growths of InP and obtained hole concentrations from $p = 3 \times 10^{16}$ to $2 \times 10^{18}$ cm$^{-3}$ at Cp$_2$Mg vapor flows of $1 \times 10^{-8}$ to $1 \times 10^{-7}$ moles/min. The doping level varied as the square of the dopant vapor flow, therefore incorporation is mass transfer controlled. At lower dopant flow rates, no Mg was detected by SIMS. They also report a diffusion coefficient (at 600°C) of $D_{\text{Mg}} = 2.4 \times 10^{-15}$ cm$^2$/sec which is based on SIMS profiles. In Blaauw et al. [60] similar "threshold-like" dopant incorporation using MCp$_2$Mg during low pressure growths (76 torr) was reported. We also observed
substrate doping-level dependent deep diffusion of Mg, a decrease in hole concentration and stacking fault formation at high Mg concentrations indicating strong compensation possibly from a Mg donor-like complex. More details of the MCp₂Mg work are presented in the following section of this text. Due to the uncontrollable super-linear incorporation rate of Mg during both atmosphere and low pressure growths, and the compensation and layer morphology degradation at high [Mg] for low pressure growths, Mg may be unsuitable for certain device applications.

Zinc doping of MOCVD InP is the most often reported p-doping method. Two sources, DEZn[45,58,112] and DMZn[58], have been used in either the bubbler or diluted in a high-pressure cylinder configuration. Nelson and Westbrook[58] used both configurations (DEZn in a bubbler at 0°C and 750 ppm DMZn in H₂ in a high pressure cylinder) and reported little difference between the use of either Zn precursor. They obtained hole concentrations of p = 4x10¹⁷ to 2x10¹⁸ cm⁻³ (calculated from Hall effect data) using Zn, with a square root dependence on DEZn or DMZn vapor flow from 2x10⁻⁸ to 1x10⁻⁶ moles/min. Above 1x10⁻⁶ moles/min, the Hall hole concentration became saturated at 2x10¹⁸ cm⁻³ which is similar to the saturation level (2-3x10¹⁸ cm⁻³) reported by the other crystal growth techniques already discussed. Razeghi and Duchemin[45] observed a wider range of incorporation p = 0.2-4.0x10¹⁸ cm⁻³ from their experiments using organometallic DEZn.
They also reported that by increasing the growth temperature from $T_g = 530$ to $650^\circ$C at a fixed DEZn flow, the 300 K hole concentration decreased from $4 \times 10^{18}$ to $4 \times 10^{17} \text{cm}^{-3}$ due to, as they explain, increased dopant evaporation from the growing surface.

Nelson and Westbrook[58] also calculated the diffusion coefficient of Zn in InP based on SIMS depth profiles of atomic zinc into InP substrates coming from epitaxially grown InP:Zn layers. They report a diffusion coefficient (at $600^\circ$C) of $D_{Zn} = 1 - 6 \times 10^{-13} \text{cm}^2/\text{sec}$, which is approximately two orders of magnitude larger than the values they reported for Cd and Mg. Yang et al.[112] grew a Zn-doped InP layer by MOCVD using DEZn simultaneously on a (100) and (111B) InP:Fe substrate. The reported hole concentrations calculated from room temperature Hall data were $p = 6.5 \times 10^{17}$ and $1.9 \times 10^{17} \text{cm}^{-3}$ on (100) and (111B) orientations, respectively. Perhaps Zn adsorbs more strongly on the (100) orientation resulting in a higher hole concentration. No one reports layer morphology degradation at high doping levels of Zn. This reason, in combination with its reasonably wide incorporation range, may explain why zinc is the most often used p-type dopant. This conclusion is valid for both low-pressure and atmospheric pressure MOCVD growth of InP, even though its bulk diffusivity is quite large.
3.2 MOCVD Growth and Characterization of Mg-Doped InP Using bis-(Methylcyclopentadienyl) Magnesium as a Dopant Source

3.2.1 Introduction

Epitaxial layers of Mg doped (p-type) InP have been grown by the low pressure MOCVD method using MCP₂Mg as a MO source. Previously, CP₂Mg doped InP has been grown by the atmospheric pressure MOCVD method[58,113]. The atomic incorporation and subsequent diffusion of Mg in InP has been determined by SIMS. The surface morphology of grown Mg:InP layers has been investigated using an optical microscope equipped with Nomarski phase contrasting and also by TEM. The electrical characteristics of the layers were measured by the Van der Pauw Hall effect technique and by an electrochemical C-V profiler. The optical characteristics of the layers were also measured by PL at 7 K.

3.2.2 MOCVD Growth

The Mg-doped InP crystal growth was performed by this investigator in a commercial (CVT, Ltd.), custom designed, MOCVD reactor at BNR in Ottawa, Canada. The organometallics TMIn and MCP₂Mg were used and kept at 17°C, 800 torr and 22°C, 700 torr, respectively. Fifteen percent phosphine diluted in UHP hydrogen was also used as a source gas. The carrier gas was hydrogen and the total H₂ flow rate was electronically controlled to be 7 SLM. A radial manifold existed at the inlet to the horizontal quartz reactor. The reactor was held at a pressure of 75 torr and RF inductively heated to a growth
temperature of 625°C. A deflector and baffle were used in the reactor to improve both the gas mixing and the gas flow pattern, respectively. A TMIn mole fraction of \(0.7 \times 10^{-4}\) and a V/III ratio of 140 were used for the growths. Both S-doped \((n \approx 8 \times 10^{18} \text{cm}^{-3})\) and Fe-doped (semi-insulating) (100) oriented InP substrates were used. Prior to loading into the reactor, the substrates were mechanically polished using a bromine-methanol solution, rinsed in methanol, and blown dry with filtered high purity nitrogen. Clean quartzware (the liner tube and gas deflector) was used for each individual MOCVD growth and the graphite susceptor was baked-out before each series of experiments to aid in experimental accuracy and reproducibility.

3.2.3 Results and Discussion

3.2.3a. Mg Incorporation and Layer Morphology

The atomic Mg concentration profile in the InP:Mg layers was determined by SIMS using \(^{157}\text{CsMg}^+\) molecular ions with a \(^{24}\text{Mg}\) implant as a standard. A representative SIMS profile of growth B232 is shown in Figure 38. During this growth, the flow rate of hydrogen through the MCP\(_2\)Mg bubbler was 12.5 sccm and this resulted in a \([\text{Mg}] = 3 \times 10^{18} \text{cm}^{-3}\), atomic magnesium concentration. All of the magnesium doped layers had a growth rate of approximately 1.0 μm/hour; independent of magnesium concentration. Figure 39 shows the effect of the \(\text{H}_2\) flow rate through the MCP\(_2\)Mg bubbler on the atomic Mg concentration in the layers determined by SIMS. An interesting feature of this
Figure 38: Atomic magnesium SIMS profile of sample B232 which was grown on a S-doped InP substrate.
Figure 39: The effect of H$_2$ flow rate through the bubbler on [Mg] as determined by SIMS.
plot is the rapid increase of the Mg concentration with a small change in the H₂ flow rate. This unfortunate phenomenon has also been reported from Mg doping of GaAs, using the MCP₂Mg source[114].

At low Mg concentrations smooth layers were grown, but at a concentration of 10¹⁹cm⁻³, the surface morphology started to deteriorate as witnessed by the appearance of stacking faults. The morphology at a particular Mg concentration was similar for layers grown on Fe-doped and on S-doped InP substrates. Several samples were investigated by TEM, using both plan view and cross-sectional samples. No features indicative of increased defect densities or precipitates could be detected at any Mg doping level below 10¹⁹cm⁻³, but at higher doping levels stacking faults were found up to a density greater than 10⁹cm⁻².

3.2.3b Mg Diffusion in S-doped InP Substrates

Figure 40 shows SIMS profiles of Mg for layers grown at different Mg doping levels on S-doped substrates. In addition to the Mg in the epilayer, Mg spikes, like the one clearly seen in Figure 38, were observed at the epilayer/substrate interface, with a subsequent rapid decay of the Mg signal to the instrumental detection limit, at ≈ 10¹⁵cm⁻³. For layers grown with a high Mg doping concentration, ([Mg] > 3x10¹⁹cm⁻³), a Mg concentration of ≈ 10¹⁹cm⁻³ was attained in the doping spikes, independent of the Mg level in the as-grown epilayer.
Figure 40: SIMS Mg profiles of InP layers on S-InP (symbols represent H₂ flow rates of 5, 12.5, 22 and 27.5 sccm to the Mg bubbler, respectively).
In Blaauw et al. [115], results were presented on the diffusion of Zn in InP. It is proposed that the presence of sulfur and silicon donor atoms in InP can act as traps and immobilize zinc. As shown in Figure 40, apparently magnesium can also be trapped up to a level corresponding to the substrate donor concentration \( (n=1\times10^{19}\text{cm}^{-3}) \). Also the depth of diffusion (1 to 2 microns) appears to be determined by the total amount of Mg diffusing across the substrate/epilayer interface and depends on the diffusion time (one hour) and the epilayer doping level.

The increase in Mg concentration with epilayer depth for the Mg profile at the lowest doping level in Figure 40 was observed in all low concentration Mg-doped layers grown on both S-doped and Fe-doped substrates. This phenomenon may be related to a Mg gas phase depletion reaction which occurs with an increasing rate as the reactor wall gradually gets coated.

**3.2.3c Mg Diffusion in Fe-doped InP Substrates**

The atomic Mg concentrations of InP:Mg layers grown on InP:Fe substrates were the same as the layers simultaneously grown on InP:S substrates. The Mg diffusion depths however were much greater, up to 32\( \mu \text{m} \) deep for the layers grown on InP:Fe substrates. The SIMS profiles for four different samples are shown in Figure 41. As shown, similar to the diffusion in InP:S, the Mg is immobilized but at a lower level of \( 10^{17}\text{cm}^{-3} \) and then drops off abruptly to the instrumental detection limit \( (\approx 10^{15}\text{cm}^{-3}) \). The \( 10^{17}\text{cm}^{-3} \) plateau must be
Figure 41: SIMS Mg profiles of InP on Fe-InP (symbols represent \( \text{H}_2 \) flow rates of 5, 12.5, 22 and 27.5 sccm to the Mg bubbler, respectively).
related to the substrate iron doping level ($0.3 - 10 \times 10^{17} \text{cm}^{-3}$) and suggests the existence of an immobile Fe-Mg complex.

### 3.2.3d Electrical Characteristics

Electrochemical C-V profiling measurements were carried out for layers grown on S-doped substrates, and flat profiles were typically obtained. A typical C-V profile is shown in Figure 42. As shown, the hole concentration for this sample, growth B229, is $p = 2 \times 10^{18} \text{cm}^{-3}$ and the layer thickness is roughly one micron. The hole carrier concentration determined by C-V profiling is shown in Figure 43 as a function of the Mg (SIMS) concentration in the layers. Up to a concentration level of $[\text{Mg}] \approx 2 \times 10^{18} \text{cm}^{-3}$, an approximately linear relationship between C-V profile hole concentrations and SIMS measured atomic Mg concentrations (on both S- and Fe-InP) was observed. As $[\text{Mg}]$ was increased further, the net hole concentration gradually decreased from a maximum value of $p \approx 2 \times 10^{18} \text{cm}^{-3}$ to a value of $p \approx 8 \times 10^{16} \text{cm}^{-3}$ $[\text{Mg}] \approx 3 \times 10^{19} \text{cm}^{-3}$. This suggests that at high levels, Mg is acting as a donor, compensating InP.

Hall measurements were performed on layers grown on Fe-doped substrates but the results were not considered reliable due to the uncertainty in depth from the extended diffusion of electrically active Mg atoms. Electrochemical C-V profiling, using the front contact method, was also performed on the InP:Fe layers. The SIMS and C-V results for a sample doped at $[\text{Mg}] = 2 \times 10^{18} \text{cm}^{-3}$ are shown in Figure 44. The agreement between SIMS and C-V profiles confirms that all the Mg is
Figure 42: C-V profile of growth B229 (InP:Mg on InP:S).
Figure 43: The relationship between atomic [Mg] and hole concentration for InP:Mg layers.
Figure 44: SIMS and hole concentration profiles of InP:Mg grown on InP:Fe.
electrically active, including that of the diffused Mg at the $[\text{Mg}] \approx 10^{17}\text{cm}^{-3}$ plateau. Similar profiles for a highly doped sample are presented in Figure 45, and show that in the surface region of the epilayer, where $[\text{Mg}]$ is high, a much lower hole concentration is measured. This result is in agreement with the relationship between $[\text{Mg}]$ and the hole concentration as observed for layers on S-doped substrates at high $[\text{Mg}]$ (Figure 43).

3.2.3e Photoluminescence Results

The low temperature PL of the Mg doped InP is shown for several dopant concentrations in Figure 46. The nominally undoped (n-type) material shows strong donor and free exciton (D-X) recombination at 874 nm; in addition we see weak band to acceptor (Zn, e-A) transitions, at 900 nm, related to residual Zn contaminants[116]. As small quantities of Mg are added, acceptor-bound excitons (A-X) at 877 nm become apparent[116] and the dominant e-A transition shifts from 900 nm (e-Zn) to 896nm, corresponding to e-Mg acceptor transitions[117]. In the middle Mg concentration range, the e-Mg transition broadens and becomes dominant. At $[\text{Mg}] > 2 \times 10^{18}\text{cm}^{-3}$ the spectra consist of a single broad peak. At the same nominal excitation conditions, the peak occurs at higher wavelengths as $[\text{Mg}]$ increases. This trend may be related to the existence of compensating donors at high Mg concentrations as suggested by C-V measurements.
Figure 45: Mg and hole concentration profiles of InP:Mg on InP:Fe.
Figure 46: PL spectra of InP:Mg layers measured at 7K.
3.2.4 Conclusions

The use of MCP_2Mg as a p-dopant source for MOCVD InP has been investigated and the Mg incorporation was found to be non-linear. For Mg concentrations above 10^{19} \text{cm}^{-3} the layer morphology deteriorated (stacking faults were observed by TEM). Extended diffusion of the Mg in the grown layers into both InP:S and InP:Fe substrates was observed. It appears based on the shapes of C-V and SIMS profiles, that immobile Mg-S and Mg-Fe complexes form in InP. At doping levels exceeding 10^{19} \text{cm}^{-3}, significant electrical compensation takes place; the net hole concentration decreases with increasing [Mg] in the layers. Because of these abnormal incorporation and doping characteristics, Mg may be considered an unsuitable dopant for InP in some device applications.

3.3 Experimental DMCd and DEZn p-Type Doping of MOCVD InP

3.3.1 Introduction

In addition to Mg which was discussed above, the use of Cd and Zn as p-type dopants for MOCVD InP has been studied while this investigator was a visitor at BNR. During these experiments, the metal organic (MO) compounds dimethylcadmium (DMCd) and diethylzinc (DEZn) have been used as Cd and Zn sources, respectively. The effect of MO flow rate on layer morphology, atomic incorporation and electrical activation in InP has been determined by Nomarski optical microscopy, SIMS, Hall and C-V measurements. For DEZn, the effect of varying
the V/III ratio and growth temperature on material properties has also been studied. The ultimate goal of this work was to find the overall "ideal" p-type dopant for InP based devices grown in the BNR low pressure MOCVD system.

3.3.2 DMCd Results

The DMCd doping experiments were carried out in the CVT Ltd. MOCVD system which was discussed in section 3.2.2. The InP:Cd growth conditions were: \( P_g = 76 \text{ torr}; \ T_g = 625^\circ\text{C}; \ F_{H_2} = 7 \text{ SLM}; \ V/III = 140; \) DMCd total bubbler pressure = 600 torr; and, DMCd bubbler temperature = 15.9°C (vapor pressure = 3.898 torr). The hydrogen flow rate through the DMCd bubbler was varied from 90 to 700 sccm which resulted in a DMCd molar flow rate range of \( 2.94 \times 10^{-5} \) to \( 2.284 \times 10^{-4} \) moles/min. At the higher DMCd flow rates, the material quality rapidly degrades due to the formation of large hillocks possibly from the formation of Cd-P precipitates. The hole concentration of these grown layers is plotted as a function of DMCd molar flow rate in Figure 47. Also plotted in Figure 47 is Cd doping data from the same reactor of a previous study by Blaauw et al.[59]. A linear relationship between DMCd flow rate and hole carrier concentration for both data sets is evident. The main conclusion is that at high DMCd molar flow rates grown at a low pressure of 76 torr, InP:Cd material quality is poor. This is unfortunate because DMCd has a wide incorporation range and Cd is a relatively slow diffuser in InP[58].
Figure 47: The effect of DMCd molar flow rate on InP hole concentration. The circles are data taken from Blaauw et al.[59]
3.3.3 DEZn Results

The DEZn doping experiments carried out in the BNR reactor made use of two different physical sources in order to get a wide range of source flow rates. One source was a DEZn bubbler which was kept at -15°C (vapor pressure = 0.619 torr), the other was a high pressure gas cylinder containing a mixture of 92 ppm DEZn by volume with the balance being UHP H₂. With these concentrations, and a flow rate as low as 5 sccm from the cylinder and as high as 200 sccm of H₂ through the bubbler, DEZn molar flow rates from $1.1 \times 10^{-7}$ to $4.92 \times 10^{-4}$ moles/min were attained. Unless noted otherwise, all the experiments were performed with the same basic conditions as listed for the DMCd experiments.

After the growths were completed, several methods were employed to characterize the InP:Zn thin films. The surfaces were observed under an optical microscope and for all doping levels, the grown layer morphology was smooth and essentially featureless. A SIMS profile of the atomic zinc concentration in InP:Zn sample B316 is presented in Figure 48. As shown, the [Zn] is $7 \times 10^{16}$ cm$^{-3}$ for this 1.4μm thick layer which was grown using 175 sccm of DEZn from the gas cylinder. The "spike" in the profile is probably due to a donor-acceptor complex as was observed in the InP:Mg samples. The [Zn] (SIMS) is plotted in Figure 49 versus the DEZn molar flow rate for experiments using both the bubbler and cylinder sources. It is evident that up to approximately $3 \times 10^{-6}$ moles/minute,
Figure 48: SIMS profile of atomic zinc in InP grown on InP:S (sample B316).
Figure 49: Total zinc incorporation in MOCVD InP from both bubbler and cylinder sources as determined by SIMS.
the \([\text{Zn}]\) is linearly proportional to \(\text{DEZn}\) flow rate, then, a saturation level of \([\text{Zn}] = 2-4 \times 10^{18} \text{cm}^{-3}\) exists. Also, the measured \(\text{InP}\) growth rate is unaffected by the \(\text{DEZn}\) flow rate for all of the experiments performed and, conversely, the doping level is unaffected by a change in the growth rate.

Electrical characterization of grown layers was also performed by using an electrochemical C-V profiler and by performing Hall effect measurements. A typical C-V profile of an \(\text{InP:Zn}\) growth with \(\text{DEZn}\) from the bubbler (sample B318) is shown in Figure 50. This \(\approx 2.4 \mu\text{m}\) thick \(\text{InP:Zn}\) film was also characterized by room temperature Hall effect measurements and the C-V carrier concentration, \(p = 1 \times 10^{18} \text{cm}^{-3}\), was confirmed. Some \(\text{InP:Zn}\) samples were grown with thin lattice-matched \(\text{GaInAs:Zn}\) contact layers to improve the likelihood of making ohmic contacts. After the contacts were alloyed, the thin \(\text{GaInAs:Zn}\) layer was removed by etching and Hall measurements were performed. The Hall and C-V measured 300 K carrier concentrations are plotted as a function of atomic zinc concentrations (determined by SIMS) in Figure 51. Less Hall data is shown as the results from several samples were deemed unreliable due to rectifying contacts. The hole concentration (electrically active Zn) for the highly doped samples is less than the atomic (total) Zn concentration. In other words, at high \(\text{DEZn}\) molar flow rates a fraction of the zinc atoms are incorporated into \(\text{InP}\) as either electrically neutral or possibly compensating donor defects.
Figure 50: C-V profile of sample B318 InP:Zn (bubbler) grown on InP:S.
Figure 51: The relationship between SIMS zinc concentration and hole concentration in InP:Zn.
In an attempt to obtain more information about the nature of the DEZn p-type doping process of MOCVD InP, a series of experiments were performed where the V/III ratio and growth temperature were independently varied. The V/III ratio for all of the other DEZn doping experiments was held at 140. Using a constant DEZn molar flow rate of $5.0 \times 10^{-7}$ moles/min, V/III ratios of 10, 50, 140, and 200 were used for separate p-doping experiments. In another series of growths, a higher DEZn flow rate, $2.0 \times 10^{-5}$ moles/min, was used with the same four V/III ratios. These eight samples were characterized by SIMS and C-V profiling and the resulting hole and atomic zinc concentrations are plotted in Figure 52 as a function of V/III ratio. It appears that by increasing the V/III ratios, both the hole and zinc concentrations decrease for both sets of experiments. This trend may be misleading since the phosphine source is only 15% concentrated which means that the total flow rate to the reactor increased by 200 sccm when the V/III ratio was increased to 200, and decreased by 420 sccm when the V/III ratio was reduced to 10, both relative to the base condition, V/III = 140 and phosphine mixture flow of 457 sccm. An increase or decrease in the total flow rate does reduce or increase the relative DEZn partial pressure in the reactor for a fixed DEZn molar flow rate. It's also interesting to note that, as plotted, the ratio of hole to zinc concentration is less for the high [Zn] runs than it is for the low [Zn] runs, indicating less electrical activation.
Figure 52: The effect of V/III ratio on Zn incorporation and hole concentration.
The effect of MOCVD growth temperature on atomic zinc incorporation was also studied. Layers of InP p-doped using DEZn at a fixed molar flow rate of $2.0 \times 10^{-6}$ moles/min were grown at temperatures from 550 to 680°C. The effect of growth temperature on atomic incorporation as determined from SIMS profiles is plotted in Figure 53. As shown, the atomic Zn incorporation drops from $4 \times 10^{18} \text{cm}^{-3}$ to $5 \times 10^{17} \text{cm}^{-3}$ as the growth temperature is increased. This is the same trend that was previously discussed and reported for DEZn doping[45] and DMCd doping[58]. This trend indicates a build up of DEZn, or some species containing zinc, near the InP:Zn growing surface which has a temperature dependent equilibrium vapor pressure. Hence, at higher temperatures, more zinc evaporates from the surface, or stays in the gas phase, and less gets incorporated into the solid.

3.4 Modeling of p-type Doping of InP using DEZn

3.4.1 Introduction

Effective control of p-type doping in InP grown by MOCVD is important in many solid state devices such as lasers, photodetectors, and heterojunction bipolar transistors. The process of p-type doping is not fully understood at this time. A model explaining this process could be useful in selecting a suitable dopant and/or proper doping conditions for a wide range of optoelectronic device applications. Experiments have been performed at BNR and at the University of Florida on the use of the MOs dimethylcadmium (DMCd), diethylzinc (DEZn) and...
Figure 53: The effect of growth temperature on Zn (from DEZn) incorporation in InP.
bis-(methylcyclopentadienyl) magnesium (MCp₂Mg) as sources for the p-type doping of MOCVD InP. A summary of the measured hole concentration versus dopant partial pressure relationship for each of these three dopants is presented in Figure 54. Using the definition of an "ideal" p-type dopant given in section 3.3.1, the information given in sections 3.3.2 and 3.3.3, and the data shown in this figure, it is clear that DEZn is the best p-type dopant for MOCVD InP grown at a low pressure. Consequently, the experimental data and other information gathered from the literature review on DEZn doping of InP will be used to formulate a model of the p-type doping process of MOCVD InP.

Bulk crystal zinc doped InP has been grown by the LEC method[101]. Epitaxial layers have been grown from the liquid phase by LPE[103] and the gas phase by hydride[109], chloride [110] and metal organic[45,58] CVD. Zinc doped crystals or layers grown using these different techniques have been reported to have approximately the same following dopant incorporation and electrical activation relationship relative to the dopant source concentration: (1) zinc has a solubility limit in InP of 2-4×10¹⁸ cm⁻³, and then forms ZnP; and (2) once this solubility is attained, at higher source concentrations measured hole concentration levels sometimes remain constant and sometimes decrease. For LEC grown bulk crystals[101], the decrease in 300 K hole concentration has been attributed to precipitates without substantial evidence. Wada et al.[103]
Figure 54: The effect of dopant partial pressure on hole concentration for InP:Mg, InP:Cd and InP:Zn.
state that a decrease in hole concentration at higher zinc melt concentrations is due to compensation in the form of an interstitial zinc donor complex originally proposed by Hooper and Tuck[104]. Hydride CVD grown material has been reported to increase and then decrease in hole concentration with the number of experiments performed using the same indium-zinc heated source[109]. This writer proposed that this trend is due to a coupling of zinc compensation and evaporation. Chloride CVD grown samples with initially low zinc electrical activation, became, upon annealing, fully active[110]. This can be explained by the disassociation of compensating defect complexes due to prolonged heating. Finally, MOCVD grown samples saturate at \( p = 2 \times 10^{18} \text{cm}^{-3} \) and the hole concentration has a square root dependence on DEZn partial pressure[58].

As the MOCVD growth temperature is increased, hole and atomic zinc concentrations decrease due to increased zinc evaporation from the growing surface at higher temperatures [45]. Most of the above trends for MOCVD grown InP:Zn have been observed in the BNR DEZn doped InP data which is shown in Figure 55. Note that at low \([\text{Zn}]\), \( p \approx [\text{Zn}] \), but above \([\text{Zn}] = 2 \times 10^{17} \text{cm}^{-3} \), \([\text{Zn}] \) eventually becomes much greater than \( p \). In addition, for the BNR data, the low growth rate of undoped InP, one micron per hour, was unaffected by the DEZn molar flow rate even at its maximum, \( 4.92 \times 10^{-6} \) moles/min, and the hole concentration was unaffected by a change in growth rate at a fixed DEZn flow rate.
Figure 55: SIMS and hole concentration data for InP:Zn which is used for the model evaluation.
The degree of electrical activation in zinc doped InP does vary with the amount of atomically incorporated zinc and this phenomenon has been investigated by several research teams. Williams et al.[118] have used proton-induced X-ray emission (PIXE) combined with channeling techniques to analyze Zn-doped InP. They concluded that neutral complexes such as $V_pZn_{In}V_p$, (which was first proposed by Hooper and Tuck[104] based on external diffusion experiments), do not exist but nonsubstitutional Zn is in the form of randomly distributed precipitates. More recently, Lennard et al.[119] performed PIXE experiments on Zn-doped InP and found no evidence for precipitates, but state that $V_pZn_{In}V_p$ complexes could explain electrical inactivation. Yamada et al.[120] theorized that the neutral complexes $V_pZn_{In}V_p$ and $Zn_{In}V_p$ exist in InP:Zn and that their presence explains the double diffusion fronts observed by electron beam induced current (EBIC) and SIMS analysis of their externally zinc diffused samples.

Interstitial zinc, $Zn_i$, both positively charged as a compensating donor, $Zn_i^+$, [121,122] and as an intermediate reacting with substrate donor atoms to form a neutral complex[123], have also been proposed to explain Zn diffusion profiles in InP. Another report states that interstitial zinc must be electrically neutral[124] based on the shape of simulated diffusion profiles taking the charge of $m$, of $Zn_i^m$, to be 0, +1, +2. Kazmierski[124] also suggests that other
theories which set \( m = 1 \), or 2 do not take into account the effect of substrate doping on zinc diffusion.

In addition to PIXE, EBIC, SIMS and diffusion theory, other techniques have been employed to investigate the InP:Zn activation phenomenon. Positron lifetime measurements have been performed on InP:Zn crystals by Dlubek et al.[125]. They report that the crystal doped with Zn to a concentration of \( 4.5 \times 10^{18} \text{cm}^{-3} \) shows strong positron trapping by vacancy defects, but no vacancies are found in crystals doped with Zn to a lower concentration of \( 2 \times 10^{18} \text{cm}^{-3} \) or doped with Sn, S or Fe. They also state that the existence of the complex \( V_pZnInV_p \), which is a deep unionized acceptor, is in perfect agreement with their positron results. DLTS has also been performed on InP:Zn and a hole trap with an energy of \( E_{v'} = 0.52 \text{eV} \) was observed[126]. The trap's origin is attributed to either a phosphorus vacancy or a phosphorus interstitial related defect. Kamijoh et al.[127] performed 4.2 K PL on undoped InP grown by MOCVD at different V/III ratios. They conclude that Zn and C-acceptor impurity incorporation is controlled by the V/III ratio. The effect of post growth cooling ambient on the electrical activation of Zn and Cd dopants in MOCVD InP has also been studied[128,129]. Cole et al.[128] reported nearly complete activation in samples cooled in \( \text{H}_2 \) only, intermediate activation (\( \approx 50\% \)) in samples cooled in \( \text{PH}_3 \) and \( \text{H}_2 \), and low activation (\( \approx 10\% \)) in samples which cooled to room temperature with \( \text{AsH}_3 \) and \( \text{H}_2 \) flowing. They rule out the existence of the
$V_pZn_{i_n}V_p$ complex based on their results and propose that atomic hydrogen which comes from the pyrolysis of the hydrides, has an influence on the doping level of p-InP. They support this theory by showing that SIMS H-profiles are related to doping profiles. Glade et al.\cite{129} performed annealing experiments and they proposed that acceptor-hydrogen complexes exist interstitially and their activation is limited by indium vacancy diffusion. Also, hydrogen passivation of a p-type InP:Mn sample showed a drastic decrease in hole concentration from $p = 7.4 \times 10^{16}\text{cm}^{-3}$ down to $p \approx 10^{13}\text{cm}^{-3}$\cite{130}. So, it is clearly evident that there is still much uncertainty about the electrical activation process of p-dopants in InP.

3.4.2 Point Defect Structure

The incorporation of DEZn during the growth of InP by MOCVD can be explained qualitatively by the model of Razeghi and Duchemin\cite{45}. The first assumption is that all the DEZn arriving at the growing surface is decomposed. This is a good assumption since the growth temperature is usually 600-650°C and the onset of pyrolysis of DEZn occurs at 332.3°C\cite{131}. Hence, the Zn concentration is limited by the rate of arrival of DEZn to the hot surface. After decomposition there are two possible limiting cases proposed by Razeghi and Duchemin\cite{45}: (1) all of the available decomposed dopant source material is incorporated into the growing layer and the resulting impurity concentration is independent of temperature and inversely proportional to the growth rate; and (2) only a small fraction
of the Zn dopant is incorporated into the growing layer and
the rest evaporates and is transported away from the growing
crystal. If the growth temperature is raised, the dopant
evaporation rate increases and consequently, the fraction
incorporated decreases. Also, the doping concentration would
be independent of the growth rate. The behavior described in
case (2) is typical of DEZn doping of InP as observed for
MOCVD growth at BNR, the University of Florida and also
reported in the literature (see sections 2.5.2c, 3.1.5c, and
3.3 of this text).

Several different point defects and defect complexes have
been proposed to explain the apparent electrical inactivity of
incorporated zinc in InP:Zn. These point defects and other
host crystal point defects such as a phosphorus vacancy, \( V_p \),
and an indium vacancy, \( V_{In} \), are represented in a fictitious
two-dimensional InP lattice which is shown in Figure 56. The
relative concentrations of these defects in a real crystal
depends upon the conditions for which it was grown and the
environment it is presently in. Chemical reactions can be
written for each point defect, and traditional methods of
chemical engineering thermodynamics can also be used to derive
expressions for the concentrations of neutral and charged
point defects and complexes. The assumption will be made that
the concentration of these point defects is small relative to
the host crystal atomic concentration. This will simplify the
equations required. Temperature-dependent equilibrium
Figure 56: Schematic representation of point defects in zinc doped InP.
constants can also be obtained from experimental data or from estimates based on values of similar materials. Hurle has previously applied the point defect analysis in a series of papers on undoped[132], tellurium doped[133], tin doped[134], and germanium doped[135] GaAs. To this writer's knowledge, this technique, applied to InP, has never been reported before. This method has been used to understand the relative concentrations of the point defects of InP:Zn which are shown in Figure 56. Anti-site defects (In_p and P_in) may also exist, but it is assumed that their concentrations are small relative to the other defects already being considered.

As stated previously, formation and ionization equations and equilibrium constants can be written for the point defects in InP:Zn. If the concentrations of the defects considered are small, then it is safe to assume that their activities are equal to their concentrations (activity coefficients are unity), except for electrons and holes. Also, if defect concentrations are small, then the activities of P_p, In_in, V_i would be unity. Using these conditions, equilibrium constant expressions for each reaction can also be derived. The reactions to form the host crystal and zinc related point defects and their corresponding equilibrium relations are given in Table 8 (Equations 11-21). Also given in Table 8 is the electroneutrality relation (22) which is written under the premise that all stable solids are electrically neutral.
## Table 8

**InP Point Defect Constants and Electroneutrality Relation**

### Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{4} P_{4}(g) + V_{i} = P_{i}$</td>
<td>$K_{h1} = \frac{[P_{i}]}{[P_{i}]}$ (11)</td>
</tr>
<tr>
<td>$P_{P} + V_{i} = P_{i} + V_{P}$</td>
<td>$K_{h2} = [P_{i}][V_{P}]$ (12)</td>
</tr>
<tr>
<td>$V_{P} = V_{P}^{+} + e^{-}$</td>
<td>$K_{h3} = \frac{\gamma_{p}[V_{P}^{+}]}{[V_{P}]}$ (13)</td>
</tr>
<tr>
<td>$0 = e^{-} + h^{+}$</td>
<td>$K_{h4} = \gamma_{n}\gamma_{p}np$ (14)</td>
</tr>
<tr>
<td>$In_{In} + V_{i} = In_{i} + V_{In}$</td>
<td>$K_{h5} = [In_{i}][V_{In}]$ (15)</td>
</tr>
<tr>
<td>$0 = V_{In} + V_{P}$</td>
<td>$K_{h6} = [V_{In}][V_{P}]$ (16)</td>
</tr>
<tr>
<td>$V_{In} = V_{In}^{-} + h^{+}$</td>
<td>$K_{h7} = \frac{\gamma_{p}[V_{In}^{-}]}{[V_{In}]}$ (17)</td>
</tr>
<tr>
<td>$Zn(g) + V_{i} = Zn_{i}$</td>
<td>$K_{d8} = \frac{[Zn_{i}]}{p_{Zn}}$ (18)</td>
</tr>
<tr>
<td>$Zn(g) + V_{In} = Zn_{In}^{-} + h^{+}$</td>
<td>$K_{d9} = \frac{\gamma_{p}[Zn_{In}^{-}]}{[V_{In}]p_{Zn}}$ (19)</td>
</tr>
<tr>
<td>$Zn_{In}^{-} + V_{P}^{+} = Zn_{In}V_{P}$</td>
<td>$K_{d10} = \frac{[Zn_{In}V_{P}]}{[Zn_{In}^{+}]V_{P}^{+}}$ (20)</td>
</tr>
<tr>
<td>$P_{P} + Zn_{In}V_{P} = V_{P}Zn_{In}V_{P} + P_{i}$</td>
<td>$K_{d11} = \frac{[V_{P}Zn_{In}V_{P}][P_{i}]}{[Zn_{In}V_{P}]}$ (21)</td>
</tr>
</tbody>
</table>


\[ n + [V_{In}^{-}] + [Zn_{In}^{-}] = p + [V_{P}^{+}] \] (22)
The partial pressures of phosphorous and zinc, $p_{P_4}$ and $p_{Zn}$, in the gas phase near the heated InP surface are known. As already discussed, the majority of zinc in the gas phase above the growing InP:Zn crystal is not incorporated into the solid. Also, InP is typically grown with a large overpressure of PH$_3$ ($V/III = 140$) which cracks to form P$_4$. Consequently, both $p_{Zn}$ and $p_{P_4}$ are set equal to the gas phase partial pressures at the inlet to the reactor of DEZn and PH$_3$, respectively.

It has been reported that $\gamma_n$ and $\gamma_p$, the activity coefficients of the electrons and holes, are only important for closely compensated material[132], hence their magnitude is set to unity. If the eleven constants $K_{n^+} - K_{n^7}$, $K_{p^8} - K_{d11}$, are known and electroneutrality is satisfied, then the twelve unknown defect concentrations: $P_i$, $In_i$, $V_p$, $V_{p^+}$, $n$, $p$, $V_{In}$, $V_{In^-}$, $Zn_i$, $Zn_{in^-}$, $Zn_{in^+}$, $V_{pZn_{in}}$, $V_{pZn_{in}V_p}$, can be calculated. The charged state of zinc related defects have been chosen based on values reported in the literature and discussed in the previous section, and based on the observed incorporation and electrical characteristics of the InP:Zn data from BNR.

Undoped InP grown by MOCVD in the BNR reactor had a room temperature carrier concentration of $n = 1-2 \times 10^{15} \text{cm}^{-3}$. The lowest hole concentration achieved from the DEZn doping of InP experiments was $p = 2 \times 10^{16} \text{cm}^{-3}$ and most layers had much higher hole concentrations. Hence, it is safe to approximate the electroneutrality relation by its two dominant members at room
temperature (Brouwer's approximation[136]) \( p \) and \([\text{Zn}_{\text{In}}^-]\). So, a new simpler relation is realized:

\[
p = [\text{Zn}_{\text{In}}^-]
\] (23)

which only applies at room temperature. Useful SIMS data on InP:Zn samples taken at room temperature was also available. It must be assumed that zinc related defect concentrations at the growth temperature will be approximately the same at room temperature. The room temperature total zinc concentration, \([\text{Zn}]\) (by SIMS), is then given by the following equation:

\[
[\text{Zn}] = [\text{Zn}_{\text{In}}^-] + [\text{Zn}_1] + [\text{Zn}_{\text{In}}V_p] + [V_p \text{Zn}_{\text{In}}V_p]
\] (24)

The room temperature electroneutrality equation (equation 23) does not apply at the growth temperature. The full form of equation 22 in Table 8 must be used to calculated the hole concentration at the growth temperature, but it can be simplified based on an order of magnitude analysis. Hurle [132] states that group III vacancy concentration \([V_{\text{In}}]\) can be neglected relative to the group V vacancy concentration. So, the growth temperature (gt) hole equation now is:

\[
p_{\text{gt}} = n_{\text{gt}} + [\text{Zn}_{\text{In}}^-] - [V_p^+]
\] (25)
Using the equilibrium constant relationships given in Table 8, with \( \gamma_n = \gamma_p = 1 \), equations 23-25 can be solved analytically. The solutions are:

\[
P_{rt} = \frac{B_1B_2p_{zn}(Pp_4^{1/4})}{P_{gt}}
\]

(27)

and

\[
[Zn] = P_{zn} \left[ \frac{B_1B_2(Pp_4^{1/4})}{P_{gt}} + B_5 + \left( \frac{B_6B_7B_4}{B_6} \right) \left( 1 + \frac{B_7}{(Pp_4^{1/4})} \right) \right]
\]

(28)

where \( B_1 - B_7 \) are constants defined as follows: \( B_1 = K_{d9}K_{h6}, B_2 = K_{h1}/K_{h2}, B_3 = K_{h3}, B_4 = K_{h4}, B_5 = K_{d8}, B_6 = K_{d10} \) and \( B_7 = K_{d11}/K_{h1} \). It is significant to note that when equation 26 is substituted into equation 27, the expected (often reported in the literature) \( p \) versus \( p_{zn} \) square root dependency exists.

For InP, the electron-hole pair equilibrium constant, \( K_{h4}(B_4) \) can be approximated using the following equation[137]:

\[
K_{h4} = 4 \left[ 2\pi (m_em_h)^{1/2}kT/h \right]^2 \exp \left( -\frac{E_g}{kT} \right)
\]

(29)
where $m_e/m_o = 0.077$, $m_n/m_o = 0.56$, $k = 1.38 \times 10^{-23} J/K$, $T_g = 898 K$ (growth temperature), $h = 6.624 \times 10^{-34} J \cdot sec$, $E_g = 1.0536 eV$ (InP bandgap at 625°C), and $m_o = 9.11 \times 10^{-31} kg$. This value turns out to be $K_{h4}(B_4) = 4.888 \times 10^{29} cm^{-3}$. Due to the large size of this constant, all constants, $p$, and $[Zn]$ data were converted to mole fractions by a simple conversion factor. The factor (which is presented in Hurle[132]) is based on the molecular density, volume and weight of InP, and Avogadro's number. The factor is: one mole fraction $= 2.557 \times 10^{-21} cm^{-3}$. Using this factor, $K_{h4}(B_4) = 3.196 \times 10^{-12}$ mole fraction$^2$.

No direct estimate, either theoretical or experimental is available in the literature for constants $B_1 - B_3$, and $B_5 - B_7$. So, estimates were taken from the values reported for GaAs by Hurle[132]. These values were used as initial guesses in a non-linear regression analysis program based on the Marquardt method[138], which is described in the Appendix C. The experimental hole concentration data (converted to mole fractions) and their corresponding zinc partial pressures (in atmospheres) were entered into the program as data set #1. The atomic zinc data (SIMS) and their corresponding zinc partial pressures were also entered as data set #2. Both data sets were taken from the BNR data shown in Figure 55. The phosphorus partial pressure, $p_{p4} = 2.357 \times 10^{-3} atm$ (V/III = 140), was also entered as part of the equations which are shown in Appendix C. The program was run twice, once for each data set, and it basically fits the hole equation to data set #1.
and the total zinc equation to the data set #2 by adjusting the values of the unknown constants. Once convergence has been achieved, (a 95% confidence limit is met) the program stops and it prints out the fitted constants. Three constants $B_1$, $B_2$ and $B_3$ were fitted using data set #1. Three more, $B_5$, $B_6$ and $B_7$ were fitted using data set #2. The resulting values of the best fit are: $B_1 = 375.3 \text{ mole fraction}^3/\text{atm}$, $B_2 = 2.5 \text{ mole fraction}^{-1}\text{atm}^{1/4}$, $B_3 = 1.23 \times 10^{-18} \text{ mole fraction}$, $B_5 = 2708 \text{ mole fraction}/\text{atm}$, $B_6 = 1003 \text{ mole fraction}^{-1}$, $B_7 = 11.6 \text{ atm}^{1/4}$.

### 3.4.3 Discussion of Results

A comparison between the model's best fit line and the data for both data sets (p and [Zn]) is shown in Figure 57. It is encouraging to see that the hole - $p_{\text{zn}}$ square root dependence of the model does agree quite well with the C-V and Hall data. Also, the total zinc data, which has less scatter, is fit even better by the model line. It is difficult to assess the real meaning of some of the evaluated constants which are actually combinations of two unknowns. But, using the total zinc data (data set #2) and the fitted constants, one can get an idea of the relative concentrations of the proposed point defects $\text{Zn}_{\text{in}}^-$, $\text{Zn}_i^-$, $V_pZn_{\text{in}}V_p$, and $Zn_{\text{in}}V_p$ as a function of zinc partial pressure. These relationships are plotted in Figure 58. As shown, the point defect model which was proposed, indicates that at low zinc partial pressures, $\text{Zn}_{\text{in}}^-$ makes up the majority of the total incorporated atomic zinc ($p_{\text{zn}}[\text{Zn}]$). As the zinc partial pressure is increased,
Figure 57: A comparison of the model (solid lines) and the experimental data for InP:Zn.
Figure 58: InP point defect distribution based on the model results.
electrically inactive interstitial zinc, Zn\textsubscript{i}, and the complex V\textsubscript{p}Zn\textsubscript{i}nV\textsubscript{p} gradually increase in relative concentration as Zn\textsubscript{i} decreases (p < [Zn]). The model also shows that the complex Zn\textsubscript{i}nV\textsubscript{p} is essentially non-existent at all zinc partial pressures.

The trends shown in Figure 57 agree very well with the theories upon which the model was developed. However, other theories such as compensation due to ionized interstitial zinc and zinc-hydrogen passivation must also be evaluated by developing new model equations. Also, this work would be more convincing if less constants had to be fitted to experimental data. Unfortunately, InP has not received as much attention in the literature as GaAs and, consequently, little or no information on lattice dilation or high temperature Hall effect measurements are available. Perhaps future researchers can fill these important gaps. This method could also be applied to understanding the effects of varying the growth temperature and the V/III ratio on zinc incorporation in InP and extend the model to analyzing cadmium and magnesium doping of InP. Hopefully by completing this puzzling topic with the aid of modelling, an "ideal" p-type dopant for InP will eventually be found.
CHAPTER IV
EPITAXIALLY GROWN INTERFERENCE FILTERS

4.1 Theory of Interference Filters

If a beam of electromagnetic radiation is incident upon a structure consisting of films of different materials, multiple reflections will occur within the structure[139]. Should the distances between the various boundaries be on the order of the wavelength of the incident light, the reflected beams will interfere. An optical interference stack makes use of this effect. These stacks or periodic multilayer dielectric films find application as bandpass filters and mirrors. Usually, the multilayer is a quarter-wave stack consisting of alternating layers of high and low refractive index material with the optical thickness of each layer a quarter of the particular required wavelength. Passive interference filters have been previously grown by MBE [140,141] and MOCVD[142] in the GaAs/AlGaAs material system. They have also been grown by CBE[143] and MOCVD [87,144] in the GaInAsP/InP material system.

The most general method of calculating the transmittance and the reflectance of a multilayer is based on a matrix formulation of the boundary conditions of the film surfaces derived from Maxwell's equations[145]. Basically, a two by
two matrix is formed from the refractive index, $n$; thickness, $t$; angle of incidence of light of wavelength $\lambda$, $\theta$; and, angle of propagation of light, $\phi$, for each of the layers (see Figure 59) in the stack. The resulting matrix for layer $j$ is as follows:

$$
\begin{bmatrix}
\cos \delta_j & \frac{i}{u_j} \sin \delta_j \\
\frac{iu_j \sin \delta_j}{\cos \delta_j} & \cos \delta_j
\end{bmatrix}
$$

(30)

where the phase $\delta_j$ is:

$$
\delta_j = \frac{2\pi}{\lambda} (n_j t_j \cos \phi_j)
$$

(31)

and $u_j$, the effective refractive index is:

$$
u_j = \begin{cases}
\frac{n_j}{\cos \phi_j} & \text{parallel} \\
n_j \cos \phi_j & \text{perpendicular}
\end{cases}
$$

(32)

depending on whether the incident light is polarized parallel or perpendicular to the plane of incidence[145]. The angle $\phi_j$ is calculated using Snell's Law:

$$
n_m \sin \theta = n_j \sin \phi_j
$$

(33)

where the refractive index of the medium (air), $n_m$, is unity.
Figure 59: Optical theory of an interference filter.
The complete multilayer of Figure 59 is represented by their product matrix, M:

\[
M = \begin{bmatrix}
m_{11} & im_{12} \\
im_{21} & m_{22}
\end{bmatrix} = M_1M_2\cdots M_l
\]

(34)

From the individual elements, \(m_{ij}\), of the matrix \(M\), the reflectivity (neglecting absorption and scattering) can be calculated as follows:

\[
R = \frac{(n_m m_{11} - n_s m_{22})^2 + (n_m n_s m_{12} - m_{21})^2}{(n_m m_{11} + n_s m_{22})^2 + (n_m n_s m_{12} + m_{21})^2}
\]

(35)

where \(n_s\) is the refractive index of the substrate material. A computer program based on equations (30) to (35) which was written to calculate the reflectivity as a function of wavelength for both GaAs and InP based stack structures. Within the program, estimates of the refractive indices (RI) of \(\text{Al}_x\text{Ga}_{1-x}\text{As}\) and \(\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}\) materials were calculated at photon energies below the direct band edge. The RI values are based on semi-empirical formulas of Afromowitz[146] for \(\text{Al}_x\text{Ga}_{1-x}\text{As}\) and of Broberg and Lindgren[147] for \(\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}\).

For quarter-wave films the number of periods of high and low RI layers required to attain a desired reflectivity can be calculated using the following equation from Born and Wolf[145]:
$$R = \frac{1 - \frac{n_2}{n_1}\left(\frac{n_2}{n_1}\right)^{2N}}{1 + \frac{n_2}{n_1}\left(\frac{n_2}{n_1}\right)^{2N}}$$  \quad (36)$$

where \(N\) is the number of layer pairs and \(n_1, n_2\) are the layers as shown in Figure 59. It is important to note that if \(n_2/n_1\) decreases and/or \(N\) is increased, \(R\) increases. Also, a larger value of \(R\) will be realized if the stack is ordered such that \(n_2/n_1\) is less than unity. It is significant to note that lower values of the \(n_2/n_1\) ratio will also result in narrower central bandwidths. The GaAs/AlGaAs material system was used because of its compatibility with optoelectronic devices. Results of GaAs/AlGaAs interference filters are presented in the next section of this text. All GaAs/AlGaAs layers were grown by MBE at BNR.

MOCVD grown GaInAsP/InP material was also investigated and the results of filters grown from this material system are presented in section 4.4.3 of this document. The quaternary MOCVD system at the University of Florida is equipped with sources making it possible to grow thin alternating layers of \(\text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y}\) and InP for interference filter structures. This is significant because with the lattice-matched GaInAsP/InP material system, a lower refractive index ratio (\(n_2/n_1 = 0.9042\)) is possible (with light at 1300nm) than with the GaAs/AlGaAs system (minimum ratio of 0.9240). This makes it
theoretically possible to get a higher reflectivity for the same number of layers using GaInAsP/InP material system.

4.2 MBE Grown AlGaAs/GaAs Devices

4.2.1 Introduction

A novel optoelectronic structure is presented, based on an optical interference filter with a stack of quarter-wave p-n heterojunctions in the GaAs/AlGaAs III-V semiconductor system. Combining these passive filters with multiple p-n junctions to introduce electrical functions, to the best of our knowledge, has never been reported before. Such devices can be used as a passive optical filter as well as active optoelectronic switch elements.

Since $\lambda = 1300$nm is a wavelength of interest in fibre-optic communications, it was chosen as the central peak reflectivity wavelength. For quarter-wave films, the number of periods of high and low RI layers required to attain a desired reflectivity can be calculated using equation (35). Useful estimates of the room temperature refractive indices (RI) of AlGaAs at photon energies below the direct band edge can be calculated from a semi-empirical formula of Afromowitz[146]. The pertinent values used at a wavelength of 1300nm are: $n$(GaAs, $E_g=1.42$eV) = 3.408 and $n$(Al$_{0.3}$Ga$_{0.7}$As, $E_g = 1.827$eV) = 3.251. A typical structure of 20 periods of 97.5nm GaAs/ 102.5nm Al$_{0.3}$Ga$_{0.7}$As (see Figure 60) with an expected peak reflectivity of 84% was chosen (see equations (31) - (35)).
Figure 60: A typical layer structure grown by MBE.
4.2.2 Electrical Theory

The RI of a semiconductor can be modulated by changing any one of several physical parameters[148]. Of primary interest here are the electrically controllable ones, i.e., the applied electric field (Franz-Keldysh effect) and the free carrier density. The former has been reported[141], but direct application of the high voltages necessary for obtaining the electric field gave rise to excessive leakage currents, which introduced thermal drift of the optical properties.

The object of this work is to apply the high electric field found in p-n heterojunctions to achieve modulation of the RI without having to resort to high applied voltages. Introducing a p-n junction into every period of the stack, however, implies that every other junction will be reverse-biased upon application of an external voltage. Thus, the possibility of excessive power dissipation and attendant thermal effects may be reintroduced if attempts are made to pass current through the device, e.g., to inject carriers.

However, the thickness of layers determined by the optical requirements (only 100nm) allows neighboring junctions to interact, as in the bipolar transistor. The stack can then be considered as a multi-layered thyristor with at least two stable switching states achievable. The forward voltage in the "ON" state can be substantially lower than the breakdown voltage of any single reverse-biased junction and can also be
accompanied by light emission if there is sufficient carrier injection.

The novel active optoelectronic switch element thus created has the useful feature of indicating its state optically at a wavelength (e.g. 870nm) remote from the wavelength the element is switching by means of its altered reflectivity response (e.g. 1300nm). As with thyristors in general, switching between the "ON" and "OFF" states can be controlled either electrically or optically.

The electronic structure of such a multi-heterojunction stack is very complex. Simple analysis indicates, that to achieve bistability, the number of junctions must be even [149]. More detailed analysis is required to optimize the modulator function, as well as to design the stack for a given forward breakdown voltage and holding current. With an appropriate design, the emitted light could also be involved in the switching function by way of optical feedback.

4.2.3 Experimental
4.2.3a Crystal Growth

The superlattice was grown by periodic variation of the Al content in epitaxially grown AlGaAs crystals on a GaAs (001) substrate using a VG - Semicon V80-H molecular beam epitaxy (MBE) system. The 2" diameter substrate was rotated during growth and was prepared for indium-free mounting using previously described methods[150].
Layers were grown at the substrate temperature of 670°C using the oxide removal temperature as a reference[151]. The GaAs growth rate was \( \approx 1 \mu m/hr \) and the Al flux was adjusted to achieve the 30% AlAs composition in AlGaAs. As\(_2\) was the arsenic source and the V/III flux ratio was maintained between 3 and 5.

4.2.3b Transmission Electron Microscopy

Shown in Figure 61 is a transmission electron microscopy (TEM) photograph of a cleaved (110) and etched edge of the stack. The alternating dark and light delineated layers represent GaAs and AlGaAs, respectively. As shown, the interfaces are abrupt and from this photo it is evident that the structure has good vertical period uniformity. At 210,000 times magnification, the average GaAs/As\(_x\)Ga\(_{1-x}\)As layer pair thickness was measured to be 192nm which is very close to the design value of 200nm.

4.2.3c Double Crystal Diffractometry

Three parameters completely determine an Al\(_x\)Ga\(_{1-x}\)As - GaAs superlattice: \( t_1 \), the thickness of the GaAs layer, \( t_2 \), the thickness of the AlGaAs layer and \( x \), its composition. Double crystal rocking curves give information on \( x_v \), the layer composition of a virtual crystal having this as an average composition and \( T \) the total period thickness. The averaged composition, \( x_v \), is easily calculated from the angular spacing between the substrate peak and the main superlattice peak reflection (or zero order peak). XRD from a material in which
the lattice parameter is subject to a one-dimensional modulation is characterized by satellites around each Bragg peak of the average lattice and the total period thickness can be calculated from the angular spacing of these satellite peaks $\Delta \theta$.

A superlattice cannot be completely characterized by experimental rocking curve data alone since this yields only two ($x$ and $T$) of the three necessary parameters. Additional information is needed, which can be obtained in one of several ways. The complementary data can be obtained experimentally by making additional measurements of the optical reflectance, or PL, otherwise the individual layer thicknesses can be measured directly by cross-sectional TEM. Alternatively, since the intensities of the rocking curve satellite peaks are proportional to the layer thicknesses, they can be found interactively by fitting intensities of calculated rocking curves to the experimental ones.

The rocking curves were recorded for the (004) reflection on a modified Bede 6" double crystal diffractometer in the parallel (+,-) setting using CuK$\alpha$(\(\lambda=1.5418 \text{\AA}\)) radiation. A GaAs (001) single crystal was used as the first crystal: this crystal when rocked with an identical one gave a rocking curve FWHM of 10±.3 arc-sec. The rocking curves were simulated using a dynamical scattering theory based solution of the Takagi-Taupin equations, using the method discussed in detail by Hill[152].
Figure 61: TEM cross-section photo of a cleaved (110) and etched edge of stack MBE464.
The layer structure for the interference filter as shown in Figure 60 has a very large (≈200nm) period so that the satellite peaks are very closely spaced (≈100 arc-sec) and can only be resolved by double crystal XRD. The experimental rocking curve is shown in Figure 62. The epitaxial superlattice structure is of high quality as demonstrated by the very large number of diffraction peaks which can be observed on either side of the main substrate peak: up to five orders of diffraction on the low angle side and up to 12 on the high angle side. The average period thickness calculated from the fringe spacing is 200nm. The average AlAs concentration in the superlattice, $x_v$, as calculated from the angular spacing between the substrate and zero-order peak is 17%, which corresponds an aluminum concentration of $x=0.34$ in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

Figure 62 also shows a simulated rocking curve which is based on a dynamical scattering theory that is presented in Hill[152]. This curve was generated using the TEM determined value for $t_1/t_2$. It is encouraging to note that the simulation does show the correct general trends; the satellite peaks are decreasing in intensity with both increasing and decreasing angle. It even predicts the much lower intensity satellites for the low angle side and the alternating high and low intensity for the even and odd numbered satellites on the high angle side.
Figure 62: Experimental and theoretical DCD rocking curves.
Spectral Scanning

The experimental set-up used to measure the reflectivity of the device (see Figure 63) consisted of a tungsten halogen lamp, a chopper \((f=400\text{Hz})\), a 200mm focal length monochromator with a 600 lines/mm grating, some focusing elements, a lock-in amplifier, and a filter to separate the first and second order of the monochromator exit light. The detector used was a calibrated BNR 250FE GaInAs p-i-n. A computer operated the monochromator and lock-in via a GPIB interface, and collected and stored the data for subsequent analysis. Reflectivity values were measured over the wavelength range of 850 to 1600nm. This was the useable range for the PIN reference detector operating with a +5 volt reverse bias. The raw data was stored and later normalized by division with calibration data for the detector.

Spectral scans were performed at 3 radial positions of the two inch wafer (2, 6, and 11mm from the center). The wavelength position of the central peak maximum changed as a function of radial position due to the well known drop-off of growth rate towards the edge of a wafer caused by slight collimation of the gallium and aluminum beam fluxes incident upon the substrate. Also, the aluminum and gallium flux distributions have different drop-off rates resulting in a variation of the ternary composition away from 30% AlAs.

A change in composition means that the refractive index and optical thickness will change accordingly. This was
Figure 63: Spectral scanning system for reflection, transmission and photoresponse measurements.
observed experimentally by the increasing shift of the position of the central peak away from $\lambda=1300\text{nm}$ as the distance from the wafer center increases ($\lambda=1260$, 1225, and 1140nm, respectively) with a corresponding drop in the peak reflectivity (0.75, 0.70 and 0.65, respectively).

The theoretical reflectivity spectrum (calculated using a program based on equations (30) – (35)) and the experimental one for $\lambda=1300\text{nm}$ at 45° incidence are plotted in Figure 64. The dashed curve is the experimental data with a baseline which lies approximately 0.05 below the theoretical $R=0.30$. As shown, the experimental and theoretical spectra agree quite well for the forty-layer AlGaAs/GaAs stack.

A small piece of the wafer was cleaved and its back side was polished to a near defect-free (mirror-like) surface. For this sample, after a reflectivity scan was performed, the detector was moved (see Figure 63) to respond to light transmitted through the sample. As shown in Figure 59, theory predicts that the position of the peak of the reflectivity and valley of the transmission scans should occur at the same wavelength. These two scans are plotted in Figure 65 and as shown, the agreement with theory is quite good.

4.4 Electrical Testing

Part of the MBE 464 wafer was processed for electrical testing purposes. A blanket zinc diffusion from the top to the first p-layer was performed. Part of this zinc diffused sample was characterized by the SIMS technique. Atomic zinc
Figure 64: Theoretical (solid) and experimental (dashed) reflectivity spectra taken from wafer center.
Figure 65: Reflectivity and transmission (dashed) spectra taken near the edge of the wafer.
and aluminum profiles were measured to assess the abruptness of the AlGaAs/GaAs heterostructure interface and to determine the depth of the zinc diffusion. The profiles for the full stack structure are shown in Figure 66. As shown, both the heterojunction interface is abrupt and the Al composition is constant throughout the stack. The extent of zinc diffusion can be more clearly seen in Figure 66. It appears that the zinc diffusion ends in the second GaAs layer, hence creating the desired PNPN (even number of junctions) type structure.

After the zinc diffusion was completed and confirmed by SIMS, a Si$_3$N$_4$ dielectric coating was evaporated to a thickness of 200nm. Fifty micron square devices were delineated by etching mesas and ohmic contacts were made to the top layer. The back side of the substrate was lapped down and polished and a gold ohmic contact layer was evaporated onto this surface. The whole PNPN structure was then tested.

Individual devices were electrically probed using a HP 4145B semiconductor analyzer. Current was measured as a function of forward and reverse bias. Some devices exhibited a shift from an "OFF" to "ON" state under forward bias conditions when a voltage of 15 to 30 volts was applied. This is the first reported switch for an electrical structure of this size (forty layers). An I-V plot of a typical PNPN device exhibiting bistability is shown in Figure 67. Also plotted on the same scale is the resistance versus voltage.
Figure 66: SIMS profiles of aluminum and zinc in MBE 464.
Figure 67: I-V and R-V characteristics of a PNPN device demonstrating bistability.
As shown the current remains fairly low up to 12 volts, but then begins to increase. At a current of \(27\text{mA} (V_{th} = 12\text{ volts})\) the device turns "ON", negative resistance results when the neighboring junctions interact and the voltage drops to 3 volts. If the current is held above \(i_{\text{hold}}\), equal to 30mA for this device, the device will stay "ON", as shown. This represents a relatively high power dissipation, which can degrade the device performance by thermal drift and non-uniform current injection.

A similar device was fabricated without the added zinc diffusion step, giving a NPN (odd number of junctions) type structure. As predicted by Katz[149] this structure does not show bistability. A typical I-V and R-V of this device is shown in Figure 68. The current is low, substantially less than in the PNPN case. For this reason the NPN structure does not appear to be suitable for RI modulation by the carrier injection method.

Photoresponse measurements were performed on the PNPN device by focusing the monochromator exit light onto some electrically probed samples. The photoresponse measurement was done at normal incidence (\(\theta=0^\circ\)) and the spectra were not corrected with respect to the monochromator output. The response was measured directly at the lock-in amplifier (see Figure 63). The spectral response of the PNPN device used as a detector has a large peak at \(\approx 850\text{nm}\) due to absorption occurring primarily in GaAs, as shown in Figure 69.
Figure 68: I-V and R-V characteristics of a NPN device.
Figure 69: Photoresponse spectrum for a PNPN device.
The spectral photoresponse of the NPN device used as a detector shows two peaks at 650 and 850nm (due to Al\textsubscript{0.3}Ga\textsubscript{0.7}As and GaAs absorption, respectively) of opposite polarity (see Figure 70). The relative intensity of the peaks varied according to the position probed on the wafer. The absolute intensity was also dependent on the device selected and on the alignment of the optical system, but it was much lower than in the PNPN device. It resembled the appearances of two opposing detectors almost canceling each other's response. Since no response was observed at longer wavelengths (1000-6000nm) as expected and shown in Figure 69, the PNPN device has great potential as a tuneable electro-optic device with either electrical or optical control.

Using the RI results of Sell et al.[153] and Cross and Adams[154], at typical electrical testing conditions (20 volts through a 50 micron square device) a change in carrier concentration from $10^{16}$ to $10^{18}$cm\textsuperscript{-3} would result in a 0.8% decrease in the refractive index of the narrow band GaAs. This would result in a 10nm peak shift and a 30% drop in intensity for reflected light at 1300nm. As indicated above, the presently achieved high switching currents precluded optical measurement of the expected spectral shift due to non-uniform current distribution in the sample and heating effects. One approach to the high switching current problem is to redesign the PNPN junction stack to lower $i_{\text{hold}}$. Alternatively, all the p layers and n layers can be connected
Figure 70: Photoresponse spectrum for a NPN device.
together respectively to allow parallel operation with RI modulation capability, but no switching function.

4.2.5 Conclusions

A functional interference filter operating at a central wavelength of \( \lambda = 1300 \text{nm} \) has been fabricated from the GaAs-AlGaAs material system by MBE. The stack was doped alternately p- and n-type hence creating a novel optoelectronic switch element. The I versus V characteristics were measured and as predicted, only the PNPN device demonstrated electrical bistability. As a detector, photocurrent measured for the PNPN device peaked near the GaAs bandgap and changed direction as a function of wavelength for the NPN device. As expected, neither device showed any photoresponse for wavelengths greater than 1000nm.

The expected spectral shift of the reflectivity in response to current modulation could not be verified because of local thermal shifting of the characteristics resulting from the relatively high holding current measured in these unoptimized PNPN devices. Multiple quantum wells are also being considered to take advantage of electric field effects. The p-n junctions can also be operated in a parallel mode, (with side contacts) circumventing the necessity to switch the thyristor structure (inherent in the series mode) to the "ON" state in order to achieve RI modulation by carrier injection.
4.2.6 Addendum

Another structure, similar to the one of MBE 464, was grown with the goal of reducing the number of electrical p-n junctions in the interference stack. The actual layer structure requested for growth MBE 572 is shown in Figure 71. With this doping profile, the number of grown p-n junctions is ten instead of twenty-one, as was the case for the as grown MBE 464 sample. With less p-n junctions, the holding current and threshold voltage for this thyristor could be much less which could improve its switching characteristics.

A TEM photograph of a cleaved (110) and etched edge of sample MBE 572 is shown in Figure 72. Similar to MBE 464, the vertical period uniformity and interface abruptness appears to be quite good. However, at 50,000 times magnification, the AlGaAs/GaAs layer pair thickness was measured to be 172nm which is considerably lower than the design value of 200nm. This was later shown to not significantly affect the passive optical device performance of this interference filter. Reflectivity values were also measured on MBE 572 over the wavelength range of 850-1600nm. The normalized reflectivity data is plotted in Figure 73. Interestingly enough however, even though the layer thicknesses according to TEM are off for this structure, the central peak reflectivity is higher (0.825) than it was for sample MBE 464. Perhaps the optical alignment was better for this sample. The location of the central peak maxima, 1250nm, is also extremely good.
<table>
<thead>
<tr>
<th>Layer</th>
<th>Composition</th>
<th>Doping Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>975 Å</td>
<td>GaAs:Si(n = 5×10^{17} \text{ cm}^{-3})</td>
<td></td>
</tr>
<tr>
<td>1025 Å</td>
<td>Al_{0.3}Ga_{0.7}As:Si(n = 2×10^{17} \text{ cm}^{-3})</td>
<td></td>
</tr>
<tr>
<td>975 Å</td>
<td>GaAs:Be(p = 2×10^{17} \text{ cm}^{-3})</td>
<td></td>
</tr>
<tr>
<td>1025 Å</td>
<td>Al_{0.3}Ga_{0.7}As:Be(p = 2×10^{17} \text{ cm}^{-3})</td>
<td></td>
</tr>
<tr>
<td>1050 Å</td>
<td>GaAs buffer</td>
<td></td>
</tr>
<tr>
<td>1050 Å</td>
<td>n^+ GaAs</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 71:** MBE572 targeted structure.
Figure 72: TEM micrograph of a cross-section of the stack structure MBE572.
Figure 73: Reflectivity spectrum for sample MBE572.
Part of sample MBE 572 was processed for electrical testing purposes following the procedure previously outlined for MBE 464. A blanket zinc diffusion from the top to the first p-AlGaAs layer was performed and a SIMS profile of the atomic zinc and aluminum concentrations is shown in Figure 74. As shown, the zinc diffusion ends in the fourth layer which should be p-type AlGaAs, and the aluminum concentration in the AlGaAs layers is essentially constant. Further processing and device testing of MBE 572 is planned. Unfortunately, this investigator had to leave BNR to pursue other interests such as MOCVD growth of III-V semiconductors.

4.3 MOCVD Grown GaInAsP Devices

Optical interference filters using the GaInAsP/InP material system have been previously grown by the MOCVD technique[87,144] and also by CBE[143], but all devices were passive. As of the time of this writing, GaInAsP/InP interference filters with electrical properties, which could be used as active optoelectronic switch elements, have never been reported. Similar to GaAs, the RI of \( \text{Ga}_x\text{In}_{1-x}\text{As}_y\text{P}_{1-y} \) is affected by a change in carrier concentration. A change in carrier concentration from \( 10^{16}\text{cm}^{-3} \) to \( 10^{18}\text{cm}^{-3} \) for GaInAsP (\( \lambda g = 1400\text{nm} \)) using sub-bandgap light at a wavelength of 1550nm, would result in a change of RI of \( \Delta n_{\text{quat}} = -0.43\%[155] \). For a 30 layer quarter-wave thick structure of \( \text{Ga}_{0.375}\text{In}_{0.625}\text{As}_{0.81}\text{P}_{0.19} \) and InP with RI estimates from Broberg and Lindgren[147] of
Figure 74: SIMS profiles of zinc and aluminum from a portion of the MBE572 stack structure.
\( n_{\text{quat}} = 3.47 \) and \( n_{\text{InP}} = 3.17 \), and using equations (31), (33) and (36), a peak reflectivity of 0.9197 occurring at \( \lambda = 1550\text{nm} \) is expected. If the RI of the quaternary layer is reduced by \( \Delta n = -.015 \), the stack will no longer be exactly a quarter-wave (optically) thick. Hence, the new reflectivity peak will occur at \( \lambda = 1543\text{nm} \) and have a maximum value of 0.9090. A theoretically predicted spectrum (neglecting GaInAsP and InP absorption) for a 30 layer stack structure of alternating 1550nm quarter-wave thick layers of \( \text{Ga}_{.375}\text{In}_{.625}\text{As}_{.81}\text{P}_{.19} \) and InP is shown in Figure 75. If the central peak in Figure 75 was shifted by 7nm due to a change in the RI of the quaternary layer, a maximum change of intensity of 30% for reflected light at 1525nm (the steepest point of the peak) is expected. This optical change can be electrically controlled hence potentially creating a switching element.

A \( \text{p-GaInAsP/n-InP} \) interference filter structure was grown by MOCVD. The layer structure and growth conditions of MOCVD sample Q240 are shown in Figure 76. This sample was sent to BNR for optical testing as a passive interference filter. The reflectivity versus wavelength spectrum for sample Q240 is plotted in Figure 77. As shown, the central peak occurs at a wavelength of \( \lambda_o = 1400\text{nm} \). The detected reflectivity signal was not normalized with respect to the detector's response for this spectrum. The central wavelength is considerably different from the expected value of 1550nm. This indicates that either the growth rates, quaternary composition, RI
Figure 75: Theoretical reflectivity spectrum for sample Q240 (neglecting GaInAsP absorption).
Layer Structure

\[ \begin{align*}
1142 \text{ Å} & \quad \text{Ga}_{0.375}\text{In}_{0.625}\text{As}_{0.81}\text{P}_{0.19}:\text{Zn} (p = 5 \times 10^{17} \text{ cm}^{-3}) \\
1255 \text{ Å} & \quad \text{InP:S} (n = 2 \times 10^{18} \text{ cm}^{-3}) \\
& \quad \text{InP:S}(8 \times 10^{18} \text{ cm}^{-3}) \\
& \quad \text{SUBSTRATE}
\end{align*} \]

Growth Conditions

Growth Temperature: 620°C
Growth Pressure: 80 Torr
Hydrogen Flowrate: 7 SLM

<table>
<thead>
<tr>
<th>Metal Organics</th>
<th>Hydrides</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MF}_{\text{TMIN}} = 0.737 \times 10^{-4} )</td>
<td>( \text{MF}_{\text{PH3}} = 211 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \text{MF}_{\text{TEGa}} = 0.335 \times 10^{-4} )</td>
<td>( \text{MF}_{\text{AsH3}} = 25 \times 10^{-4} )</td>
</tr>
<tr>
<td>( \text{MF}_{\text{DEZn}} = 0.621 \times 10^{-4} )</td>
<td>( \text{MF}_{\text{H2S}} = 0.071 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

Figure 76: Layer structure and growth conditions for MOCVD growth Q240.
Figure 77: Experimental reflectivity spectrum for sample Q240.
estimates or a combination of all three are different from the expected values used to determine the layer structure and growth conditions. To determine the possible sources of error, separate parts of the MOCVD sample Q240 were given for both TEM and High Resolution XRD analysis. Until these characterization results are available, no further MOCVD growths or device processing and testing are planned for the interference filter project.
CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

Epitaxial layers of InP, Ga$_x$In$_{1-x}$As, and Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ have been grown lattice-matched to InP by MOCVD. However, the electrical properties of undoped layers of these materials grown in the quaternary MOCVD machine were not "state of the art" or, in other words, as good as is possible considering the quality of the sources presently available. The room temperature Hall mobilities of undoped InP and Ga$_{.47}$In$_{.53}$As, (on the order of 3000 and 6000 cm$^2$/volt-sec, respectively) are lower than the highest values reported in the literature (4500 cm$^2$/volt-sec for InP[55] and 10,000 cm$^2$/volt-sec for GaInAs[65]). The room temperature carrier concentrations for undoped films are low though, $n \approx 2 \cdot 10^{14}$ cm$^{-3}$, which suggests that compensation by an incorporated acceptor impurity is a cause for the inferior mobilities. The effect of growth conditions, wafer preparation and sources used on material quality have already been investigated as possible causes for compensation. It is recommended that a phosphine purifier be purchased and installed in the MOCVD system if high purity InP, GaInAs and GaInAsP layers are required for future device applications.

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Another potential solution to the compensation problem is associated with the substrate holding mechanism. Presently, the substrate is placed on top of a quartz wafer tray during the MOCVD growth. It is conceivable that this tray is the source of compensating acceptors. The tray is cleaned and dried using the same procedure as the reactor, but, unlike the rest of the reactor, it is not baked for four hours at 950°C and kept in an air-free environment before a deposition. A clean tray is used for each MOCVD growth, but, the sample is heated by conduction through the quartz tray and part of the exposed tray is directly upstream of the sample. It is recommended that a silicon carbide coated graphite tray be purchased and used to hold the sample during the MOCVD growths of structures which require high purity undoped epitaxial layers.

A model of the p-type doping process of MOCVD InP using DEZn has been developed, yet never before reported. The results of this study are that the dominant electrically inactive point defects in zinc doped InP grown using high DEZn reactor partial pressures are interstitial zinc, $Zn_i$, and zinc complexed with a phosphorous divacancy, $V_pZn_In_V_p$. Due to the fact that very little information is available on the InP:Zn material system, several assumptions were made during the course of the development of this model. It is recommended that future researchers perform extensive characterization on undoped InP and InP:Zn, such as high temperature Hall effect
measurements and lattice parameter measurements. With this added information, it would be possible to estimate more of the unknown equilibrium constants which are required in the model. This would improve the accuracy of the unknown constants that are estimated by a non-linear regression analysis program which uses the experimental SIMS and hole concentration data. It is also recommended that other point defect reactions be considered to validate or invalidate the model which was presented in this dissertation. Mechanisms such as the formation of a hydride complex as proposed by Cole et al.[128] should be considered. In addition, the charged state of all the point defects at room temperature is another uncertainty that must be considered. The study of all the possible doping mechanisms is hence proposed. Finally, it is recommended that future researchers apply the point defect analysis technique to understanding the cadmium and magnesium doping data sets for MOCVD InP which are presented in this dissertation. Cadmium appears to have an understandable linear incorporation dependence on its precursor partial pressure, but, magnesium has a dependency that suggests strong compensation and possibly n-type conversion at high source pressures.

A novel optoelectronic device incorporating multiple p-n heterojunctions in an optical interference filter has been presented. Potential applications for this device include an electrically tuneable optical filter for optoelectronic
switching and a selective wavelength detector. Electrical bistability was observed and passive optical interference was demonstrated for this device. The combination of the two device characteristics: a peak shift in the reflectivity spectrum due to the application of an external bias, was not observed. The expected spectral shift may have been observed if the holding current was lower and/or if the current distribution was more uniform. Consequently, optimized p-n-p-n structures with fewer layers using multiple quantum wells are suggested as improvements for future researchers. Also, broad-area transparent contacts to the epilayer could improve the current channeling problem.
APPENDIX A
THEORY AND OPERATION OF THE LOW TEMPERATURE HALL EFFECT SYSTEM

A.1 Theory

If current is flowing in the x-direction in a probed semiconducting sample and a magnetic field is being applied in the z-direction, the flowing charged particles will be deflected in the mutually perpendicular y-direction. To maintain the steady-state flow of particles through the device, an electric field will be induced in the y-direction. The establishment of the electric field $E_y$, (as shown in Figure 78) is known as the Hall effect[156].

By performing an experiment, like the one mentioned above, with a known applied magnetic field ($B_z$), and current density ($J_x$), one can measure the induced voltage ($V_H$). From these values, the proportionality constant:

$$R_H = E_y / (J_x B_z)$$

(37)

can be calculated. With $R_H$, the Hall coefficient, and a previously measured value of resistivity, $\rho$, for the sample, it is now straightforward to calculate the majority carrier concentration and carrier mobility of the semiconductor. Knowledge of these two temperature dependent values is a way of characterizing the type (n or p), purity and functionality of a semiconductor.
Figure 78: The Hall effect in a semiconductor.
A.2 Sample Preparation

In order to perform Hall effect measurements, a suitable sample is needed. This semiconducting sample should be expendable as the technique used is destructive. If a 2" diameter wafer exists which needs characterization, a small .5 cm to .75 cm square piece will suffice as the working sample. This sample can be obtained by first determining the crystal growth plane which is usually indicated by a flat edge on the circumference of the wafer. Next a line must be carefully scribed in the wafer parallel or perpendicular to the flat edge. The wafer can be broken or cleaved along the scribed line. With one of the two pieces, this process should be repeated until an approximately square working sample is obtained. Since the sample can have maximum dimensions of only 1 cm², sufficient material should remain for additional characterization. It has been reported[157-162] that crystal orientation affects the Hall measurement results for all anisotropic materials. Therefore, care should be taken to establish a standard procedure to prevent misleading and irreproducible results.

After the test sample has been cut, make sure the surfaces are clean. Some samples may require cleaning with a degreasing solvent such as methanol and rinsing with distilled deionized water, others may require chemical etching and material specific techniques are described elsewhere[157]. Next, identify which surface has the deposited epitaxial layer.
of interest. Depending on the type of sample, different solders must be attached as close as possible to the four corners of the wafer. For undoped GaAs and InP, pure indium works well when cut and pressed onto the "epi" layer with a clean surgical knife. The indium dots should also be as small as possible to avoid introducing error. For other materials such as doped III-V's, Si and Ge different solders are suggested[157].

Now that the solder is in place, the sample should be placed in the alloying station on the center of the graphite heating strip. Check to see that there is a small air gap between the thermocouple and the strip. Also be careful when handling the strip as it is quite fragile. Put the "o"-ring and plexiglass dome in place and tighten the mounting bolts in a diagonal fashion. Do not tighten the bolts too much as the dome is fragile.

The next step is probably the most important in the alloying process: chamber evacuation and heating in a forming gas (10% H₂ in N₂) environment. First open the regulator valve on the forming gas cylinder so that there is about 10 psi of pressure on the flow regulator gauge. Close the line to the rough pump and open the exit line of the chamber. Place the exit line in a beaker two-thirds full of water for a visual indication of the gas flow. Open the inlet valve line to chamber so that the water in the beaker is bubbling to the point of almost overflowing (increase cylinder flow if
necessary). Next close off the inlet and exit lines and open the rough pump line. Plug in the rough pump and let it run until the vacuum gauge reads -30 psi. Open the inlet line and fill the chamber with forming gas. Then simultaneously close the rough pump line and open the exit line. Let the gas flow at the previous bubbling rate for about five minutes with the hood closed. A flowmeter was attached to the system but it added too much resistance to gas flow so it was removed.

Now that the chamber is nearly free of air, plug in the digital thermometer (Omega, model 115KC) which should read about 27°C. At this point plug in the transformer (Signal, model 10.5) turn it on, and set the dial to 55 (this system is for GaAs with indium contacts). Close the hood and while heating for about twenty minutes, make sure the gas flow rate stays approximately constant. At this point the temperature should be reading \( \approx 230°C \) (of course the sample is much hotter than the thermocouple tip) and the transformer can be turned off. Keep the forming gas flowing until the temperature reads less than 50°C consequently reducing the chance of forming an oxide layer. Let the chamber cool down close to ambient temperature before opening it and removing the sample.

The final step in the sample preparation process is the testing of the nature of the contacts. The contacts have to be of the Ohmic type to be used in the Hall effect experiment. A simple check of contact integrity can be performed on a conventional transistor curve tracer (one is available in the
microelectronics lab at the University of Florida). If all possible combinations of contacts taken two at a time yield linear current-voltage plots over a wide range of applied voltage values, then, the contacts are ohmic. If they are not all ohmic, then the alloying process must be improved by trial and error.

Having prepared a square sample with ohmic contacts and no visible wafer damage (cracks, oxide haze), then this sample must be attached to an adequate sample holder. For routine measurements (300 and 77 K), a patterned printed circuit board with metal clips is available. Samples can be mounted on the board and inserted into a dewer which rests on a wooden stand in between the magnet's two poles. The dewer could be filled with liquid nitrogen or left empty depending upon the temperature required. A sample holder was also developed for temperature dependent experiments (down to 4.2 K) which consists of three interconnecting parts: the CTI-Cryogenics model SH-14R resistivity holder, an oxygen-free copper conductive plate, and a gold coated alumina mounting plate. The resistivity holder can be rotated so the semiconductor is perpendicular to the magnetic field and is also made of oxygen free copper. The copper plate was made to fit on one face of the resistivity holder with a channel in it to hold the alumina plate.

The gold covered alumina plate is the medium by which the current and voltage leads could be attached to the four ohmic
contacts but also be isolated from each other. A one inch square by .025" thick alumina plate with a 2E-06 cm thick chromium adhesion layer and a 2E-05 cm thick gold conductive layer was obtained from Materials Research Corporation. This plate was cut into 3/8" by 1" rectangular pieces by using a Micromatic precision wafering machine equipped with a diamond impregnated blade. Onto these plates a pattern of four pads was drawn with a permanent ink marker. The plates were etched in a gold etching solution of KI:I₂:H₂O in the respective volumetric ratios 4:1:40 for ten minutes or until the gold was removed. Then the plates were etched in a one part potassium to 3 part ferrocyanide by volume solution until the gray chromium layer was removed exposing the underlying non-conductive alumina. The permanent ink was finally removed with acetone revealing four isolated gold pads. To each of these four pads were soldered a 4 cm piece of non-magnetic wire with an Amphenol Incorporated female type plug connector.

To the center of the alumina mounting plate the small semiconductor sample can be attached with a portion of Crycon grease (which does not out-gas at low temperatures). The grease keeps the wafer stuck in place to the alumina plate. A very fine 1 mil thick gold wire must be ultrasonically bound from each ohmic contact to the edge of the adjacent gold pad. Request from the operator in the microelectronics lab that the wires are as short as possible so that they can withstand higher currents before burning up. This last step completes
the sample mounting and preparation stage of the Hall effect experiment.

A.3 Experimental Hall Effect Measurements

After the sample has been mounted to the resistivity holder and the holder attached to the cold finger of the cryostat (CTI-Cryogenics, model 22), make sure that the cryostat is perpendicular to the magnetic field. The wafer should also face the right magnet pole labeled "North". Now the wire from the bottom left gold pad should be connected to the wire labelled C through a pin of the resistivity holder. Similarly, the upper left to D, the upper right to E and the lower right pad should be connected to wire F. These four wires are wrapped around the cold finger and exit through the cable connector port at the base of the cryostat. The letters C, D, E, F are the pin labels on the male mating plug. These four pins are connected to wires 4, 3, 2 and 1, respectively.

The cryostage has two lines filled with a pressurized liquid helium attached to it which should not be bent to a radius less than two feet (to avoid leaks). These lines with the aid of the compressor (CTI-Cryogenics, model SC), temperature controller (Palm Beach Cryophysics, Inc., model 4025), resistive heater (which is wrapped around the top of the cold finger) and cryostat permit the measurement of Hall voltages at temperatures as low as 4.2 K. An important note about the cryostage is that whenever it is being handled, care
should be taken to avoid unnecessarily touching its internal parts and of course disposable gloves must be worn.

Once the connections have been made to the resistivity holder, the inner heat shield should be gently slipped over the cold finger and attached to the cryostage. Next the outer shield should be placed over the heat shield while making sure that its "O" ring is in place. Now the rough pump should be attached to the closed brass valve. If the helium supply and return lines, the cryostat power line, and the ten pin mating plug are attached then the cryostage is ready for operation.

The previously discussed four sample lines should be connected to the binding posts labelled 1, 2, 3 and 4 of the aluminum shielded switching box. The switching box contains three double-pole double-throw switches, a four-pole six-throw switch, a standard 100 ohm resistor and four other binding posts for current and voltages leads. This box was built by Mrs. Grazyna Palczewska, another member of our research group, as per the design in reference[157]. It efficiently permits the acquisition of Hall voltage data by a simple routine of switching current flow through the sample and the standard resistor. The standard resistor used should be of the same magnitude as the resistance of the sample[157]. The constant current supply (Lambda, model LQ531) must be attached to the +I and -I labelled binding posts. The magnitude of the current used was always less than 5 mA which was low enough to avoid resistive heating in the sample (as indicated by
constant signal values). The voltmeter used was actually a high-quality high-input impedance electrometer (Keithley Instruments, model 614) to avoid any leakage currents and consequently increased error.

Now that all electrical connections are made, the temperature desired for measurement must be reached. This can be room temperature (300 K) or lower, but the system cannot be operated above room temperature as the cryostage contains indium seals which would melt. For temperatures below ambient, the temperature controller and compressor must be used. Basically the rough pump is first plugged in and run until the pressure gauge reads 1-2 torr. At this point close the brass valve, unplug the rough pump and slowly vent the pump and hose to 760 torr. Now turn on first the compressor, then the cold head (on the compressor) and then, last, the temperature controller. The controller must be programmed with its optimum process parameters as found and explained in its manual. It was advised that the heater plugs always be disconnected whenever the temperature readout exceeded 275 K. When the combination of helium cooling and resistive heating is operating correctly in a properly evacuated environment, temperatures below 100 K should be attained and stable in about 45 minutes. If it is not thermally stable or the outside of the cryoshield is cold with condensation occurring then either the chamber was not properly evacuated or there is a leak in the cryostage.
It was suggested that a test be performed to determine if the readout temperature is a good representation of the actual temperature of the sample. This was performed by placing a second silicon diode sensor, with the same I/V characteristics as the cold finger sensor, at the exact sample position. Its four plugs were connected temporarily to four leads from the 37 pin mating plug of the temperature controller. Since the controller is capable of displaying the temperature at both sensor locations, this experiment was fairly straightforward. The results of the test are that it takes approximately fifteen minutes for the sample location to stably reach the same temperature as the permanent sensor location.

Once the desired temperature for measurement has been reached and is stable, the magnetic field should be applied. To do this, the constant current supply (Walker Scientific, model HS525) for the magnet (Walker Scientific, model HV4H) should be turned on by pressing the power button. Next the cooling water must be turned on to a flow rate great enough to illuminate the "DC-OFF" switch (this indicates adequate flow through the current supply and magnet). Of course make sure that the exit line for the water is in the drain and there are no leaks. Also, make sure that the spacing between the magnet poles is adequate and that the poles are locked in place. Now, with the percentage of maximum current dial reading zero, press the "DC-ON" switch which will activate the current generator. At this point it is safe to slowly dial in a
percentage of maximum current. For example, with a 2" pole spacing at 50% of current and with the reversal switch illuminated, a magnetic field of about 2600 gauss should be measurable with the previously zeroed gaussmeter (Jobmaster Magnets, model 6MIA). The magnetic field will be positive in the sample when it is facing the pole labeled "North" and the "DC-ON" switch is illuminated (the "Reversal" switch is not). A calibration curve for the particular pole spacing used should be obtained on a regular basis. Operating at higher magnetic fields induces higher Hall voltages and is therefore desired. The sample should always be placed as close to the center of the magnetic field and as perpendicular to its field lines as possible.

With the sample in the proper place (shielded from light), at the right temperature, with a stable low current passing through it, with the voltmeter and magnet on, record the Hall voltage value $V_5(+I,+B)$, for example, with the switch in position 5. Then by varying the current ($+I,-I$), magnetic field ($+B,-B$) and position switch ($5,6,S$) record twelve voltage values ($S$ stands for the standard resistor reference voltage). Positions 5 and 6 pass current diagonally through the samples and consequently measure voltage across the other respective diagonal. Now with the magnetic field off, put the switch in positions 1, 2, 3, 4 and $S$ and vary the current ($+I,-I$) and record the ten resistivity voltage values $V_i$. 
A.4 Calculations

Now that the twenty-two voltage measurements have been recorded, for a sample of known thickness (the thickness of an epitaxial layer when growth is on a SI substrate) and with a value of resistance for the standard resistor used the equations of reference[157] can be used to calculated the resistivity of the semiconductor ($\rho$ in ohm-cm) and the Hall coefficient ($R_H$ in cm$^3$/coulomb), which is negative for n-type and positive for p-type samples. Then with a known Hall proportionality factor ($r = 1$ for GaAs) the charged carrier concentration (n or p) can be calculated ($\mu$ in cm$^2$/volt-sec) can be calculated as $\mu=R_H/r$. These three values ($\rho$, $\mu$ and n or p) are all temperature dependant and provide a good basis of comparison in determining the quality of a grown epitaxial film.

For investigators who are interested in extremely accurate values of $\rho$, $\mu$ and n, several references[159,161-163] present correlations for samples of non-ideal geometries and finite contact sizes. It is advised that square samples have a perimeter length ($L_p$) less than 1.5 cm and with thicknesses less than 0.1 cm. Also, the contacts should be as close as possible to the corners (or edges) of the sample and of size less than 0.01$L_p$. This author advises that if errors of 10% are tolerable then using the previously mentioned correlations are not necessary.
A.5 Conclusions

The Hall effect has been used for many years as a way of characterizing semiconductor devices. It is a reliable, reproducible method with the only real drawback being its difficult, destructive contacting procedure. For both an InP and GaAs samples which were grown and characterized by an industrial lab, the measured mobility, carrier concentration and resistivity values differed by at most 10% from the company's measured results. This shows that the described contact procedure, measurement routine and calculation method should be adequate for most applications.
APPENDIX B
OPERATION OF THE QUATERNARY MOCVD SYSTEM

B.1 SCOPE

This document pertains to the quaternary MOCVD housed in building 771 on the campus of the University of Florida.

B.2 PURPOSE

The purpose of this document is to outline the correct/safe operating procedures for the MOCVD system which is used for research on optoelectronic materials.

B.3 SAFETY

No one should operate any part of this system without prior approval of, and training by Dr. Tim Anderson. The system has its own built-in safety system which will shut down upon detecting any potentially dangerous situation. If something related to the system seems to be malfunctioning, and you are not trained to operate the system, immediately (hit the red emergency stop, advise others to leave the room with you), and contact the present operator, C. Heinz, Dr. T. Anderson (392-2591) or K. Rambo).

If a problem exists in the room such as a fire, also hit the red emergency stop button. Of course, if the reactor
explodes or you suspect a hazardous gas leak, do not wait for the MDA to turn on the whooper - leave the Surge building immediately. Do not return to the room until the emergency response team has entered the room with their Scott Air packs and solved the problem. Bottle changes, reactor tube removal and cleaning and pump oil changes should be done using the buddy system; with the dual-cylinder air system. No growth shall be performed unless at least 2 people are in the building. Always wear safety glasses while in the clean room. All operators should take part in the arsenic in urine monitoring. If you ever smell a garlic-like or rotten fish odor or sense your heart rate increase above normal (for no apparent reason), leave the room. Never start a deposition or use the bubbler baths during stormy weather. Always inform the building director that you are going into the lab and if you are planning to do a growth. The MOCVD has several sensors which light-up, flash or cause a buzzer to sound on the display panel. It has three levels of warning and corresponding actions which result depending on the level of danger to the system or operator. (see pages 25-29 of Hayakawa[164]).

B.4 PREPARATION

Check with the building operator to see if anything is abnormal today with regards to the nitrogen, hydrogen, chilled water, dry air, building power supply, and air scrubbing-monitoring. Check the status of the Advanced Concepts wet
scrubber on the back pad by turning it on. Is, the pH > 10, ORP > 100, pumping pressure > 28 psi, liquid level sufficient? If not, see scrubber manual for maintenance. Check the pressure on the inlet H₂ and N₂ lines, the hydride cylinder sources. Do we need a bottle changes or six-pack hydrogen changes? Check the water filter on the chilled water line, clean if necessary. Check the temperature of the metal organic source baths. Does growth rate or doping level changes indicate the need for a source change? Is the hydrogen purifier operating properly? Is the reactor tube clean and dry and in place? Leak tight seal? Purged with H₂. Has all source changes or maintenance been followed up by a helium leak check? Did the whole system pass the leak checking procedure? If any seal has been broken on a toxic gas line, wear air masks during first operation of that line after leak checking. How is the oil level in the roughing pumps? Does the oil need changing? Change it before and after growths. Is there a clog? Have you programmed the process controller with your desired deposition scheme? Test it. (Programming tips are available in Hayakawa[164]).

B.5 PROCEDURE

B.5.1 Introduction

Now that all the facilities are in place, all safety precautions have been followed/checked, and the materials are installed, the normal operation procedure will be outlined. It is assumed that the system has already gone through its
initial start up (leak check, bake out of graphite susceptor, scrubber N₂ purge, individual components testing). It is also assumed that the reader is familiar with the physical layout of the system (see Figure 79) and what the individual system components do. Manual valves (MV), air valves (AV), needle valves (NV) and regulator valves (RV) are all mentioned in the procedure (also see Figure 79).

B.5.1 Power Supply and Programmable Controller Explanation

Turn on the 115V and 208V circuit breakers. Turn on breakers ELB 100 and 200. After the 115 and 208V lights are illuminated, turn on fuse breakers NFB102, 112 and circuit protector CP132 which are all located inside the lower right electrical panel (when facing the front of the machine). Push the "stand by", "PC ON" then "ON" switches and then all switches, readouts and emergency sensors will begin to function. If the "ON" switch is not lit, the system will function as it stands, but all air operated valves will remain open (red light) or closed (no light) even if they are pushed accidentally. The system should be in manual mode now. For a description of edit, auto modes or how to operate the programmable controller, see Hayakawa[164]. Check reactor pressure, if not slightly greater than or equal to 760 torr, turn on RP2 and open valves from RP2 inlet towards the reactor to prevent back flow to the reactor. Completely evacuate the system, start hydrogen flow and then pressurize the system by closing AV208,9 and then opening AV204 when p = 780 torr.
Figure 79: Quaternary MOCVD flow diagram (complete).
B.5.2 Definition of the "OFF" or "OVERNIGHT" State

The complete system should be purging through valves AV200, 204 at 760 torr with hydrogen. All source MVs should be closed (metal organics, hydrides) and AV111 (nitrogen inlet) should also be closed. Roughing pumps and turbo molecular pumps should be off. The scrubber should be off, Lepel RF generator also off. Water flow to Lepel, reactor and load lock and to bubblers also all off. Hydrogen purifier should always be on. Close MV14, 24, 34, as they should always be during toxic gas flow (double check).

B.5.3 How to Grow InP on InP in the MOCVD System

Turn on the scrubber, and check the hydrogen supply on back pad. Enter the clean room and check the MDA and hydrogen detector. Flow water to the system, reset water alarm, and make the deposition program now. Turn on the MO bubbler controllers and set the temperatures. Turn off the variacs for the heat tapes. Prepare the substrates. Now put the substrates into the load-lock room. Evacuate the load-lock room and close MV102, AV109, then turn RPI and RP2 on, also open MV201, MV202, NV202 and evacuate to minimum pressure.

Flow N₂ gas into the load-lock room and close MV201, MV202, NV202, then open MV102, MV202, NV202. When the pressure of the load-lock room becomes 760 torr, close NV202, MV202, MV102. Load the substrates into the load-lock room using clean room paper and gloves, close the door tightly. Evacuate the load-lock room by opening MV201, MV202, NV202.
slowly. Flow H$_2$ gas into the load-lock room by closing MV201, MV202, NV202 and opening AV109, MV202, NV202 and when the pressure of the load-lock room becomes 760 torr, close NV202, MV202, AV109. Evacuate the load-lock two more times.

Insert the substrates to the reactor from the load-lock room (fork operation). The pressure of the reactor should be 760 torr. Open MV200 and turn the fork manipulator on. Open the fork gate valve. Open the shutter valve. Move the fork forward and put the substrates on the graphite susceptor and then remove the fork. Close the shutter valve. Close the gate valve. Close MV200. Turn off the fork manipulator and double check that MV200 is closed!

Prepare for flowing toxic gases (PH$_3$ Only for InP on InP) by first closing MV20, MV23, AV204 and then quickly evacuate the system through AV209 with RP2 on. Increase the set point of MFC20 to maximum. When MFC20 indicates almost zero sccm, close AV21, AV22 and AV23 (leave AV20 open). Adjust MFC20 to about 10 sccm (set point). Close the regulator (RV20), (turn it fully counter-clockwise).

Heat the RF filament (power on, solenoid on, RF filament on) set the pressure of the reactor to 80 torr. Increase the main hydrogen flow rates to the reactor to 7 slm (total) and to each vent line 0.5 slm also increase the H$_2$ regulator to 90 psi. Set all other flow rates to overnight flows except the PH$_3$ compensation line (set to 100 sccm), TMIn, and its compensation line (both set to 143 sccm). Adjust NV60 so PI60
reads 490 torr (indium bubbler), open AV207, adjust NV203 so the reactor is at 80 torr. Flow the MO to the vent (TMIn only). Make sure AV63 is open and AV64 is closed. Adjust the pressure of the bubblers (PI60 = 490 torr). Open the MO bubbler (at first open the outlet valve and then open the inlet valve). Close AV62 and then check the pressure of the bubbler, set it to be 500 torr and stable.

Heat the substrates by setting the controller temperature to 650°C (172R). Turn on the RF plate and power switches (auto mode). Flow the toxic gas PH₃ to the reactor for 10 minutes. Check H₂ detector point 8 and constantly monitor it. Open the PH₃ cylinder slightly and adjust the outlet pressure to 0.5 kgf/cm² (use the black gloves and keep all machine doors completely closed until all PH₃ is gone). Open AV22 and then open AV21. Set MFC20 to maximum (300 sccm). Check H₂ detector point 6 then return it to auto. Start the program in 10 minutes if the temperature is stable. Close the PH₃ cylinder at an appropriate time (this depends on flow rate and cylinder pressure), possibly before the end of the growth. Close the MO bubbler after the growth ends by first opening AV62 and then close the inlet valve and last, close the outlet valve. Reduce the flow rate of the MO to 30 sccm. End the program always 3 minutes after the MO goes to the vent. Turn off the RF power, plate switches and filament of the RF generator. When the temperature of the substrate is less than 400°C (100R), turn off the RF generator power switch. When
the temperature of the substrate is less than 200°C (50R), flow PH₃ gas to the vent. When the flow rate of the PH₃ becomes 0 sccm, purge the PH₃ line five times by opening MV20 and MV23 and then close MV23, and wait until MFC20 becomes 0 sccm. Repeat this four more times and reduce MFC20 to 30 sccm, also make a note of the time.

Pressurize the reactor to 760 torr. Close AV207 and AV209, and turn off RP2. When the reactor pressure becomes 780 torr, open AV204. Remove the sample from the reactor (30 minutes after the time noted previously) by fork operation. Remove the samples from the load-lock room by first evacuating it. Close MV102, AV109, and open MV201, MV202, NV202. Flow N₂ gas into the load-lock room. Close MV201, MV202, NV202 and open MV102, MV202, NV202. When the pressure of the load-lock room becomes 760 torr, close NV202, MV202, MV102. Repeat the evacuation and fill steps three more times then remove the substrates from the load-lock room. Repeat evacuation and fill steps one more time, then turn off RP1. Reduce the H₂ regulator to 40 psi, bleed line to 100, make all flows 0.2 slm or 30 sccm.

Wash the substrate supporter using aqua regia (3 HCl:1 HNO₃) for 10 minutes then rinse with DI for one minute then dip in the HF mix (5 DI:1 HF) for 5 minutes. Follow with a DI rinse for 15 minutes. Turn off the water flow (to the MOCVD system), silence the water alarm, open the water pressure relief into the plastic tray. Turn on the variacs for the
heat tapes and exit the clean room. Turn off the scrubber, check H$_2$ supply pressures (500 psi minimum).

B.5.4 Reactor Cleaning

Purge the reactor overnight with hydrogen after a four hour bake at 900°C and 35 torr (4 slm Hydrogen flowing to the reactor). Disconnect the water line (inlet and outlet), close all water valves. Divert gas flow by closing AV119, 125, 200 then opening AV118, 124 and turn off the heat tapes. Disconnect the thermocouple cable connector. Evacuate the reactor using RP1 through the load-lock to 3 torr. Close the doors and open slowly MV207 to let air into the reactor to a pressure of 760 torr (there is a chance that a fire may occur in the reactor tube). Repeat evacuation and fill four more times.

Using the particle masks, disconnect the reactor and thermocouple. Cover all with aluminum foil. Clean the MO inlet tube, susceptor bed and reactor immediately, using the wafer tray procedure (reactor requires 2 hours of DI rinsing though). Clean the thermocouple tube using methanol, clean room paper and a clean razor blade. Clean the exhaust area (wearing particle mask) with methanol and clean room paper. Dispose of waste in toxic waste garbage can (fill out proper forms).

Install the clean thermocouple tube, and reactor with clean graphite susceptor and susceptor bed. Before connecting
the inlet flange to the reactor, check the position of the susceptor using the fork procedure and a clean wafer tray. Adjust the position if necessary. Connect the inlet flange to the reactor using fresh VCR gaskets. Evacuate the reactor to 3 torr as an initial leak check using RP1. Helium leak check the reactor.

Flow H₂ to the reactor and use the Matheson H₂ detector at all connections. Connect the water lines using tie-wraps. Bake the reactor at 35 torr, 900°C, 4 SLM H₂ flow for four hours. Turn on the heat tapes, too. Pressurize the reactor to 760 torr, set all flows to 0.2 SLM or 30 sccm.

B.5.5 Metal Organic Source Change (TMIN as an example)

Purge the MO line overnight with 300 sccm H₂. Close all air valves on the system by hitting the red emergency stop button, and turn off the heat tapes. Evacuate the MO line using RP2 (open AV209, 202, 65, 63, 62, 61, 60 and NV60 completely in this order). Open AV111 to let N₂ flow to the MO. Close NV60 until PI60 reads 900 torr then open until PI60 reads 70 torr. Repeat this ten times, then put the bubbler at 760 torr by adjusting NV60. Close all air valves. Disconnect the bubbler using particle masks and clean room gloves (make sure bubbler valves are real tight). Install the new bubbler using fresh VCR gaskets. Repeat purge and evacuation steps five times. Evacuate the whole system using RP2 and helium leak check the bubbler connections through MV207. Pressurize the system and return all flows to 0.2 slm or 30 sccm. Turn
off RP2. Use the Matheson H₂ detector around the bubbler with the bubbler at 900 torr and hydrogen flowing. Turn on the heat tapes. Flow MO to the vent for one hour before use in a growth to remove volatile impurities.

B.5.6 Hydride Source Change (PH₃ as an example)

Close the gas cylinders tightly (using the black gloves). Purge the gas lines with H₂ (five times evacuation and fill-up) then let H₂ flow overnight. Close AV21, AV22, AV23, AV20 and pressurize the gas lines with cylinder N₂ gas and then release slowly through MV41 and RV40 to the exhaust (turn on RP1 and RP2 and close exhaust AVs). Repeat this step four more times then leave the line at 760 torr and close MV23. Prepare the new cylinder (and gasket which is necessary on H₂S cylinder only) and clean room gloves and wrenches. Put on the gas mask in a buddy system, set the MDA to sense at QMOCVD only, and seal off the clean room from normal access. Take out the old gas cylinder. Put in the new gas cylinder (use the gasket).

Pressurize the gas lines with N₂ gas up to AV20. Check for leaks with soapy water. Release the N₂ pressure through MV41 and RV40 (prevent air from entering the rest of the system). If there are no leaks then remove air masks, put MDA on auto and allow others to enter the clean room. Pressurize the gas line and then release ten times with N₂. Evacuate the gas lines, and then check for leaks with helium detector. Pressurize the line overnight with N₂ and check for any
pressure drop (note room temperature). Check for leaks with
the Matheson detector by pressurizing to 200 psi with H₂ and
open/close all MV's near the cylinder. Allow H₂ to flow at
normal conditions.

Wear air masks and evacuate others from clean room during
the first use of new cylinder (before a growth), flow gas to
vent for one hour to remove volatile impurities (of course
turn scrubber on). The cylinder is now ready for routine use,
keep cylinder cabinet doors closed at all times.

B.6 Return from an Emergency Shutdown

After problem has been solved by the team wearing air
packs, if necessary, hit "alarm reset/"BZ reset" to stop
buzzer and alarm light. Evacuate and fill the system with H₂
if necessary, five times. Do a complete "preparation" check
(see section B.4). Follow the turn-on procedure at section
B.5.2.

B.7 SHUTDOWN

Return to the "OFF" state is defined in the previous
section. For a complete shutdown, the system should be
completely purged with N₂ for 1 hour (all lines up to a closed
source - manual valves closed, that is). Now, all three
temperature baths should be shut off. Close the UHP H₂ outlet
valve and evacuate the whole system to 1 torr. Then close
MV100, AV110 and hit the red emergency stop button. Turn off
the heat tapes and skinner valve. Set the H₂ purifier
temperature to 0°C and when T < 200°C, shut off the purifier,
pressurize it with N₂ and close all four MVs. Turn off the Lepel RF generator's circuit breaker. Purge the rough pumps with N₂ also. Close the nitrogen inlet, dry air and cooling water inlet and outlet valves. Turn off electric breakers ELB100, 200, and then the MOCVD breaker. The system should now be completely off and ready for a long vacation or major renovation.

B.8 MAINTENANCE

General system maintenance is done as needed. Of course, occasionally vacuum out the glove box for dust removal and wipe down the system with a "clean room" detergent. All other maintenance steps are mentioned as either part of preparation or procedure steps.
APPENDIX C
DOPANT MODEL COMPUTER PROGRAM

As stated in section 3.3.4, a non-linear regression analysis program based on the Marquardt method was used to determine values for the equilibrium constants $B_1 - B_3$, $B_5 - B_7$. The program is not listed here due to its length (which is approximately 40 pages). The program was written by Dr. Alkis Constantinides and is available on a diskette which comes with his book, Applied Numerical Methods with Personal Computers [138]. A description of how to use the program is given in section 7-5 of the book. Briefly, regression analysis is the application of mathematical and statistical methods for the analysis of experimental data, and the fitting of mathematical models to these data by the estimation of the unknown parameters of the models. By performing statistical tests, the model can be identified or verified. The Marquardt method uses an interpolation technique which is a combination of the Gauss-Newton and the steepest-descent methods to obtain values of the parameters in the model which minimize the overall (weighted) sum of the squared residuals.

The non-linear regression program is menu-driven for data input and adjustment. To use the program, one must first derive a model and variational equations. The variational equations are obtained by taking partial derivatives of the
model equation with respect to each unknown model parameter. The program was first run to solve for the constants \( B_1, B_2, B_3 \) by fitting the hole concentration model equation (27) to the hole concentration data. The model and variational equations used for this are:

\[
Y(1) = B(1) * (2.36E-06) * X * ((B(2)^2) + B(3) * B(2) / B(4) / 0.00236)^0.5) / ((B(4) + B(1) * B(2) * (2.36E-06) * X)^0.5) \]

\[
Y(2) = (2.36E-06) * X * ((B(2)^2) + B(3) * B(2) / B(4) / 0.00236)^0.5) \]

\[
Y(2) = (2.36E-06) * X * (B(2) * (2.36E-06) * X) / ((B(4) + B(1) * B(2) * (2.36E-06) * X)^1.5) \]

\[
Y(3) = B(1) * (2.36E-06) * X * (B(2) * B(4) + 0.5 * B(1) * (B(2)^2) * (2.36E-06) * X + 0.5 * B(3) / 0.00236) / (((B(2)^2) + B(3) * B(2) / B(4) / 0.00236)^0.5) \]

\[
Y(3) = (0.5 * B(1) * B(2) * (2.36E-06) * X / B(4) / 0.00236) / (((B(4) + B(1) * B(2) * (2.36E-06) * X)^0.5) \]

\[
Y(4) = -B(1) * B(2) * (2.36E-06) * X * (B(3) / B(4) / 0.00236) + (0.5 * B(1) * B(2) * B(3) * (2.36E-06) * X / 0.00236) / (((B(4) + B(1) * B(2) * (2.36E-06) * X)^0.5) \]

\[
Y(5) = -B(1) * B(2) * (2.36E-06) * X * ( (B(3) / B(4) / 0.00236) + (0.5 * B(1) * B(2) * (2.36E-06) * X)^0.5) / (((B(4) + B(1) * B(2) * (2.36E-06) * X)^0.5)) \]
where:

\[ Y(1) = \left[ p \right]_{RT} \]  
(43)

\[ Y(2) = \frac{\delta [p]_{RT}}{\delta B_1} \]  
(44)

\[ Y(3) = \frac{\delta [p]_{RT}}{\delta B_2} \]  
(45)

\[ Y(4) = \frac{\delta [p]_{RT}}{\delta B_3} \]  
(46)

\[ Y(5) = \frac{\delta [p]_{RT}}{\delta B_4} \]  
(47)

The resulting values of the best fit are: \( B_1 = 375.3 \) mole fraction\(^3\)/atm, \( B_2 = 2.5 \) mole fraction\(^1\) atm\(^{-1/4}\), and \( B_3 = 1.23 \times 10^{-18} \) mole fraction.

The non-linear regression program was executed a second time to solve for the constants \( B_5 \) - \( B_7 \) by fitting the SIMS concentration model equation (28) to the SIMS concentration data. The model and variational equations used for the second program execution are:

\[ Y(1) = B(1) \times B(2) \times 2.36E-06 \times X \times \left( \frac{(1 + \frac{B(3)}{1.0E+31}}{\frac{B(2)}{0.00236}} \right)^{0.5} \times \left( \frac{1.0E+31 + B(1) \times B(2) \times 2.36E-06 \times X}{(1.0E+31 + B(1) \times B(2) \times 2.36E-06 \times X)^{0.5}} \right) \]  
(48)
\[ Y(2) = (1.0 \times 10^{31} + 0.5 \times B(1) \times B(2) \times 2.36 \times 10^{-6} \times X) \times \left( (1.0 + (B(3)/B(2)) / 1.0 \times 10^{31} / 0.00236) \right)^{0.5} \times \frac{B(2) \times 2.36 \times 10^{-6} \times X}{(1.0 \times 10^{31} + B(1) \times B(2) \times 2.36 \times 10^{-6} \times X)^{1.5}} \]

\[ Y(3) = 0.5 \times B(1) \times 2.36 \times 10^{-6} \times X \times \left( (2 \times B(2) + (B(3) / 1.0 \times 10^{31} / 0.00236)) / ((B(2)^2 + (B(3) \times B(2) / 1.0 \times 10^{31} / 0.00236))^{0.5}} - B(1) \times 2.36 \times 10^{-6} \times X \times \left( (B(2)^2 + (B(3) \times B(2) / 1.0 \times 10^{31} / 0.00236)) / (1.0 \times 10^{31} + B(1) \times B(2) \times 2.36 \times 10^{-6} \times X) \right)^{0.5} \right) \]

\[ Y(4) = B(1) \times 0.001 \times X \times 0.5 / 1.0 \times 10^{31} / (1.0 \times 10^{31} / B(2) / 0.00236)^{0.5} / ((1.0 \times 10^{31} + B(1) \times B(2) \times 2.36 \times 10^{-6} \times X)^{0.5}) \]

where:

\[ Y(1) = \Sigma[Zn] \]

\[ Y(2) = \frac{\partial \Sigma[Zn]}{\partial B_5} \]

\[ Y(3) = \frac{\partial \Sigma[Zn]}{\partial B_6} \]

\[ Y(4) = \frac{\partial \Sigma[Zn]}{\partial B_7} \]

The resulting values of the best fit are: \( B_5 = 2708 \) mole fraction/atm, \( B_6 = 1003 \) mole fraction\(^{-1}\), and \( B_7 = 11.6 \) atm\(^{1/4}\).
REFERENCES


Arnold John Howard was born on January 6, 1963, in Huntington, NY, which is located on the north shore of Long Island. He grew up there and graduated from Huntington High School in 1981. He then enrolled at the University of Pennsylvania in Philadelphia, Pennsylvania, and graduated in 1985 with a B.S. degree in chemical engineering. While at Penn he met Robin Lustig, another Penn Quaker, at a party that he and his friends had stumbled upon; Robin later became his wife on April 7, 1990. After graduating, the author spent six weeks in nine different countries of Europe. After all that traveling, he enrolled at the University of Virginia in Charlottesville. As part of his master's program, the author spent a summer at the Oak Ridge National Laboratory performing research on the separation of sugars. He received his M.S. in chemical engineering from UVa in January of 1987 and then went further south to begin the Ph.D. program at the University of Florida in Gainesville. The author had the good fortune of choosing a research project which involved being a visitor at Bell Northern Research in Ottawa, Canada. (Gainesville was too hot!) The author plans to work at Sandia National Laboratories in Albuquerque, New Mexico, upon completion of his Doctor of Philosophy degree in chemical engineering.
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