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RL-TR-91-138
In-House Report
April 1991

DEVELOPMENT OF A LIQUID PHASE EPITAXIAL GROWTH SYSTEM FOR FABRICATION OF INDIUM PHOSPHIDE BASED DEVICES

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 1991	3. REPORT TYPE AND DATES COVERED In-House Report

4. TITLE AND SUBTITLE

Development of a Liquid Phase Epitaxial Growth System for Fabrication of Indium Phosphide Based Devices

5. FUNDING NUMBERS

PE 62702F
PR 4600
TA 19
WU 46001912

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Rome Laboratory (ESO)
Hanscom AFB, MA 01731-5000

8. PERFORMING ORGANIZATION REPORT NUMBER

RL-TR-91-138

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

We have developed a liquid phase epitaxy system for growth of thin-film, III-V materials. We have focused primarily on InP, InGaAs, and InGaAsP growth for fabricating electro-optical devices. We have developed a standard approach for each type of growth and diagnostic techniques for characterization purposes.

14. SUBJECT TERMS

LPE, Liquid phase epitaxy, III-V, InP

15. NUMBER OF PAGES

52

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

NSN 7540-01-280-5500

Standard Form 298 (rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

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Acknowledgements

We thank A. Davis and D. Wojtowicz for their help with the Hall analysis, H. Dauplaise for her help with the photoluminescence measurements, J. Horrigan and B. Bennett for their help with the x-ray analysis, and M. Dumais for his help with the SEM. In addition, we would like to thank J. Lorenzo for his enlightening discussions.

Preface

SUMMARY

This report documents a key in-house technology development, thin-film semiconductor growth by liquid phase epitaxy (abbreviated as LPE). This growth capability will enable Rome Laboratory to develop electro-optic devices in support of the Air Force photonics initiative. Included in this report are: 1) a brief background exposition; 2) an explanation of the liquid phase epitaxy technique; 3) a system description, and 4) an explanation of the experimental method. In addition, various characterization techniques and peripheral topics relevant to device fabrication will be discussed.

Development of a Liquid Phase Epitaxial Growth System For Fabrication of Indium Phosphide Based Devices

1. INTRODUCTION

1.1 III-V Materials

Every semiconducting material has unique characteristics making it well suited for particular applications. We are interested in III-V compounds, materials composed primarily of elements from Groups III and V of the periodic table (Table 1). These materials are ideally suited for electro-optic devices, which rely on optical signals as well as electrical signals, and for a variety of other high-speed communications applications. Indium phosphide (InP) and its related ternary and quaternary systems (Figure 1) are of particular interest for many reasons; possible applications being solid-state lasers, high-speed detectors and high-power transistors. These devices can be designed for use with optical fibers at 1.3 μm (where signal dispersion is minimum) or at 1.5 μm (where signal attenuation is minimum).[1,2] InP can be used to fabricate solar cells and high-power microwave devices. InP is also attractive for

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Received for Publication 1 May 1991

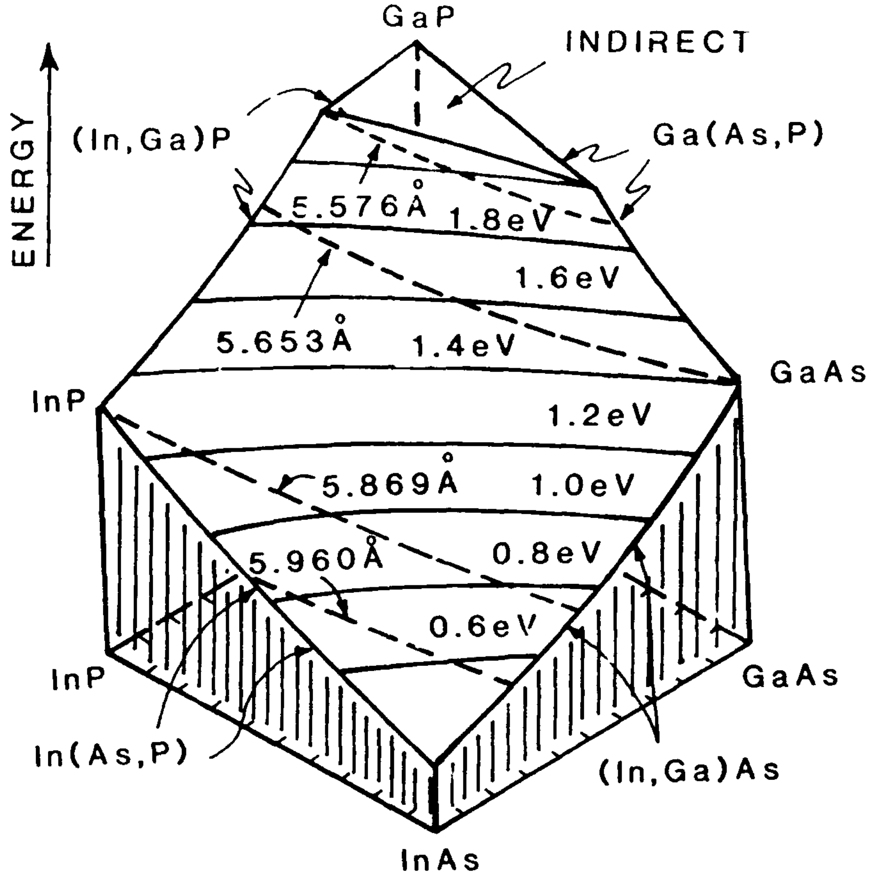
[1] Yamada, J., Saruwatari, M., Asatani, K., Tsuchiya, H., Kawana, A., Sugiyama, K., and Kimura, T. (1978) *IEEE J. Quantum Electron*, **QE-14**:791.

[2] Miya, T., Teramuna, Y., Hosaka, Y., and Miyashita, T. (1979), *Electron. Lett.*, **15**:106.

applications in environments that require radiation-tolerant components. This LPE system is used to grow III-V semiconductor thin films for the fabrication of electro-optical devices such as solar cells, photodetectors and solid-state lasers (Figures 2, 3, 4).

Table 1. III-V Compounds.

	a_o (Å)	T_m (°C)	E_g (eV)	λ (μm)	BAND STRUCTURE
AlP	5.463	>2000	2.45	0.51	INDIRECT
AlAs	5.661	1740	2.16	0.57	INDIRECT
AlSb	6.138	1050	1.65	0.75	INDIRECT
GaP	5.449	1467	2.26	0.55	INDIRECT
GaAs	5.653	1238	1.42	0.87	DIRECT
GaSb	6.095	706	0.72	1.85	DIRECT
InP	5.868	1058	1.35	0.92	DIRECT
InAs	6.058	942	0.36	3.44	DIRECT
InSb	6.479	530	0.17	7.30	DIRECT



ENERGY BANDGAP VERSUS COMPOSITION FOR (In,Ga)(As,P) QUARTERNARY ALLOYS. NEARLY HORIZONTAL SOLID CURVES ARE ISO-BANDGAP. DASHED CURVES ARE ISO-LATTICE-CONSTANT.

Figure 1. (In, Ga) (As, P) Quaternary

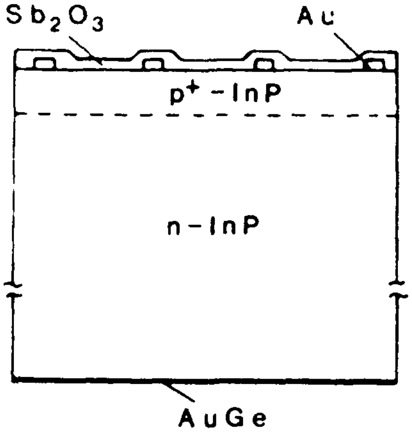


Figure 2. Cross Section of a Solar Cell

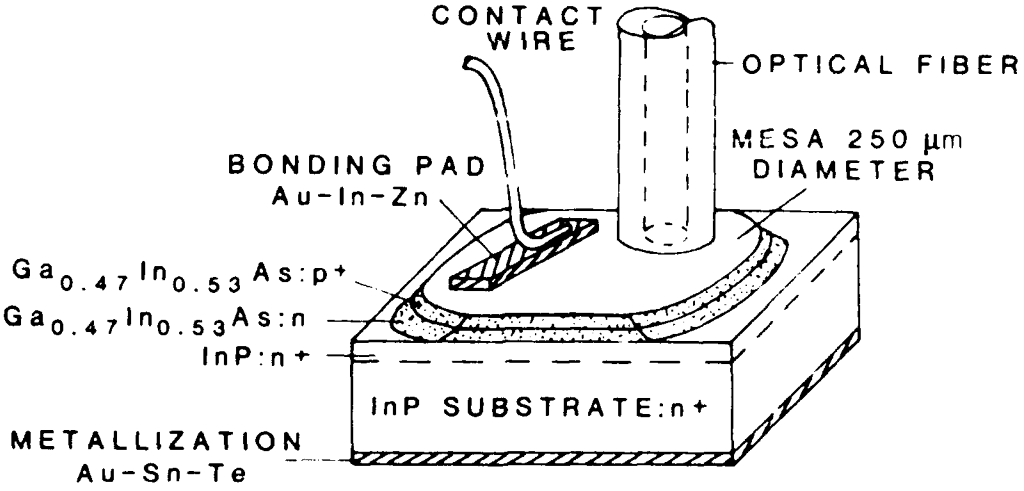


Figure 3. Photodetector

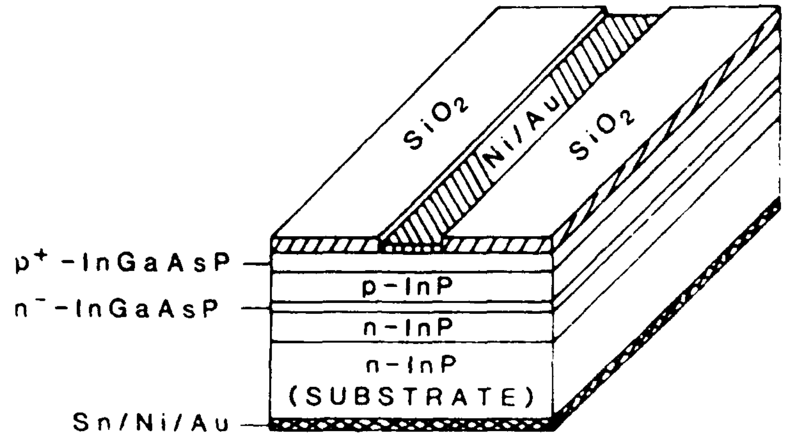


Figure 4. Quaternary Light-Emitting Diode

1.2 Epitaxial Growth

The ability to grow high-quality, epitaxial thin films is essential to the fabrication of most solid-state electronic or photonic devices. These films can be grown by a variety of methods including molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), and vapor phase epitaxy (VPE), each differing in complexity and cost. Liquid phase epitaxy (LPE) has long been considered the easiest and least expensive method of epitaxial growth on single crystal substrates for device fabrication. Its simplicity makes it ideal for basic research studies of novel device structures.

LPE material is naturally inclined to grow with very few dislocations and point defects that act as carrier traps and nonradiative recombination centers. An almost perfect lattice match between the grown layer and substrate can be obtained if the lattice constants are the same or within a few percent (for example, InP on InP). However, LPE cannot easily be used to grow films that differ greatly in lattice constant from the substrate (for example, Si on InP). Layers grown by LPE are consistently superior in optical and electrical quality. Because of the crystalline perfection that can be obtained, LPE is still used extensively to make semiconductor lasers. However, LPE has difficult growth control problems; as a result, very thin layers, like those used for quantum-well structures, are extremely difficult to grow. In addition, surface morphology is usually poorer than that obtained by other epitaxial growth methods.

The greatest advantage of the LPE method is the low system cost, in material and operational expenses. The greatest disadvantage is the lack of precise system control, leading to variation in film composition and thickness. An LPE system can be a valuable experimental tool when operated within its proper constraints. An excellent introduction to LPE can be found in *Handbook of Semiconductors*, Vol. 3.[3]

2. LPE TECHNIQUE

2.1 Basic Theory

Epitaxy is a growth process by which a thin film of material is deposited with the same crystal structure as that of an underlying substrate. The foundation for liquid phase epitaxy is the fact that the solubility of a dilute constituent in a liquid solvent decreases with decreasing temperature. Source materials (solute) are dissolved in a melt (solvent) at a given temperature until an equilibrium is reached. When the resulting solution is cooled below the equilibrium point, a saturated solution is formed. Once the solution has become fully saturated the solute begins to nucleate. When the solution is brought into contact with the substrate, epitaxial growth proceeds by spontaneous, heterogeneous nucleation at the solution/substrate interface. Equilibrium diagrams, which plot melt phase as a function of melt composition and temperature, are useful tools in determining the exact point to initiate growth. The liquidus line on an equilibrium diagram is a continuum of points where, for a particular melt composition and temperature, the liquid and solid phases are in equilibrium.

2.2 Growth Parameters

LPE growth is controlled by a combination of the following parameters: substrate crystal orientation, solution composition, growth temperature, growth time, and cooling scheme. For III-V semiconductor growth, substrate crystal orientation is usually limited to (111) or (100) surfaces. These orientations have different surface kinetics and require slightly different approaches for successful growth. As a result, the crystal orientation is usually specific for a particular LPE system.

For binary (two constituents) thin films, solution composition is always constant. Ternary and quaternary (three and four constituents) thin films may have a wide range of solution compositions that will produce a lattice-matched layer. Epitaxial films of different composition (InP, InGaAs, InGaAsP) require different combinations of the growth parameters

Growth of layers at high temperatures (700° C) may require different techniques than growth of layers of similar composition at lower temperatures (500° C). Temperature is varied to take advantage of the best possible combination of solid solubility and diffusion

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[3] Hsieh, J. (1980) Liquid Phase Epitaxy, *Handbook of Semiconductors*, Vol. 3, North-Holland Publishing Co.

coefficients. For example, high temperatures are desirable for InP growth because the diffusion coefficient of phosphorus in the melt increases with temperature, allowing more phosphorus to be supplied to the substrate/solution interface. However, growth of InP over a layer of InGaAsP must be performed at low temperatures to prevent the InGaAsP from dissolving into the melt.

Growth time, usually a function of growth temperature, varies with different materials. Growth of some thin films is reaction rate-limited, requiring shorter growth times. Others are limited by the amount of material that can be supplied to the solution/substrate interface, requiring longer growth times.

The cooling scheme has four basic options: equilibrium cooling, supercooling, stepcooling, or two-phase cooling (see Figure 5). The equilibrium scheme employs a constant, low cooling rate throughout the run. This downward temperature ramp is established before the liquidus temperature is reached. The substrate and solution are brought together when the liquidus temperature is reached, so that they are in equilibrium when contact is made. Equilibrium is maintained by cooling at the same constant rate until growth is terminated.

The supercooling scheme also employs a constant cooling rate throughout the run: however, the substrate and solution are slowly cooled to a temperature below the liquidus temperature before growth is initiated. Cooling below the liquidus temperature causes the melt to become supersaturated. Cooling by constant rate is continued until growth is terminated.

The stepcooling scheme requires the substrate and solution to be cooled below the liquidus temperature and held at a constant temperature. They are brought into contact and held at the same temperature until growth is terminated. If the substrate and solution remain in contact long enough at the constant temperature they will come into equilibrium and the growth will stop.

In the two-phase scheme, the substrate and solution are cooled at a constant rate far enough below the liquidus temperature to allow spontaneous precipitation to occur before growth is initiated. The desired growth materials are present in the melt in both liquid and solid phase.[4] During growth, the temperature can be ramped down as in equilibrium cooling or can be held constant as in the stepcooling scheme.

With careful control of these parameters, layers can be grown reproducibly to sub-micron thicknesses suitable for a variety of experimental and commercial device structures.

2.3 Growth Methods

Many variations of the LPE growth technique are available, including tipping, dipping, and sliding. The tipping method employs a horizontal furnace containing a quartz tube. The tube provides a protective environment for a graphite boat containing the growth solution and substrate (Figure 6). To initiate growth, the furnace containing the tube is tipped so that the

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[4] ibid.

melt runs over the substrate. To terminate growth, the furnace is brought back to the original position so that the melt runs off the substrate.

The dipping method employs a vertical reactor that surrounds a quartz tube. The substrate is suspended, in the tube, above a crucible containing the melt. Growth is initiated by lowering the substrate into the crucible and terminated by removing the substrate (Figure 7).

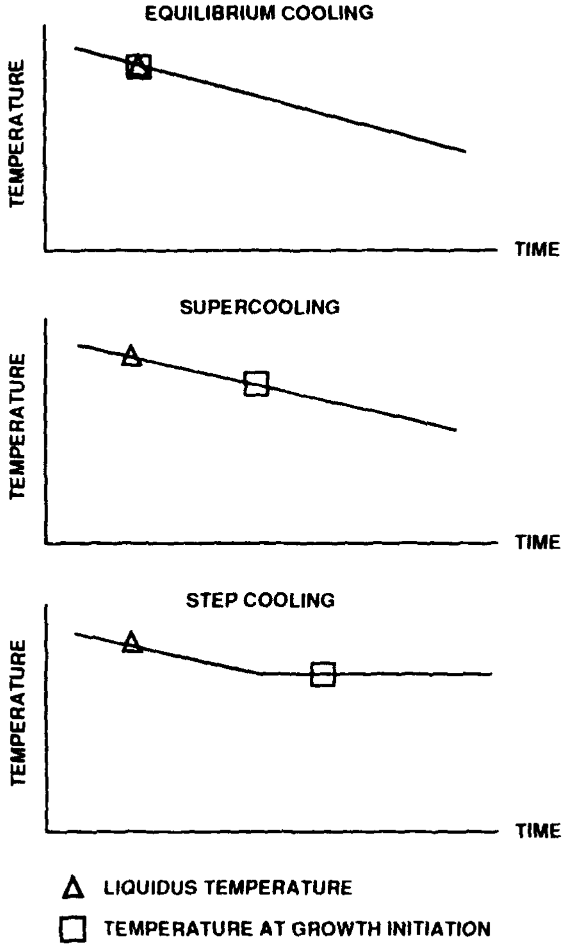

Figure 5. Cooling Schemes

The sliding technique employs a multibin, graphite slider located on a graphite boat (Figure 8) into which the growth solutions are loaded. The graphite boat is protected by a quartz tube that is inserted into a horizontal furnace. During growth runs, at the appropriate temperature, each solution is pulled over the substrate in succession. At the conclusion of the growth, any excess solution remaining on the surface is pulled along by the surface tension of the melt and pushed off by the sides of the bin. The biggest advantage of the sliding method is that is has the capability to grow multiple layers with different compositions in a single growth run.

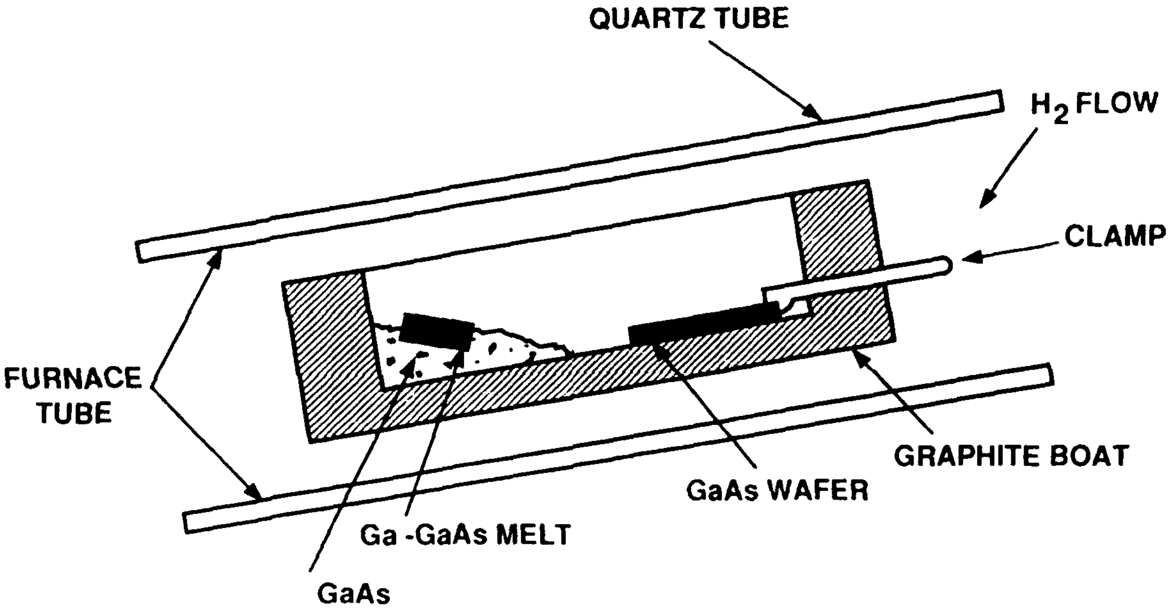

Figure 6. Tipping Method

3. SYSTEM DESCRIPTION

We have chosen to use the sliding technique because we are interested in fabricating devices that require multiple layers and some degree of thickness control. This growth technique is uncomplicated and relatively easy to learn. The heart of the system is a graphite boat surrounded by a sealed quartz tube that maintains a clean and protective environment (Figure 9).

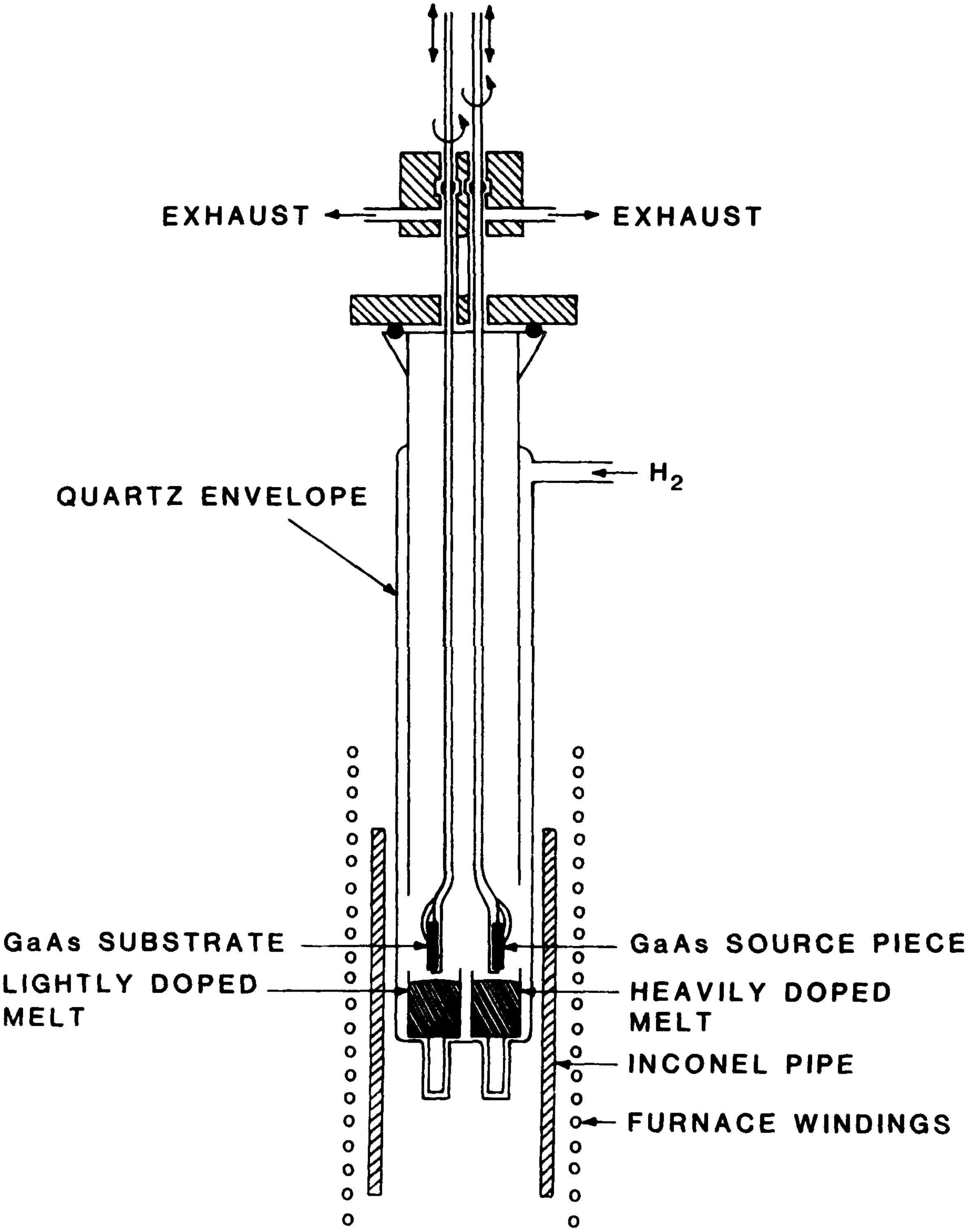

Figure 7. Dipping Method

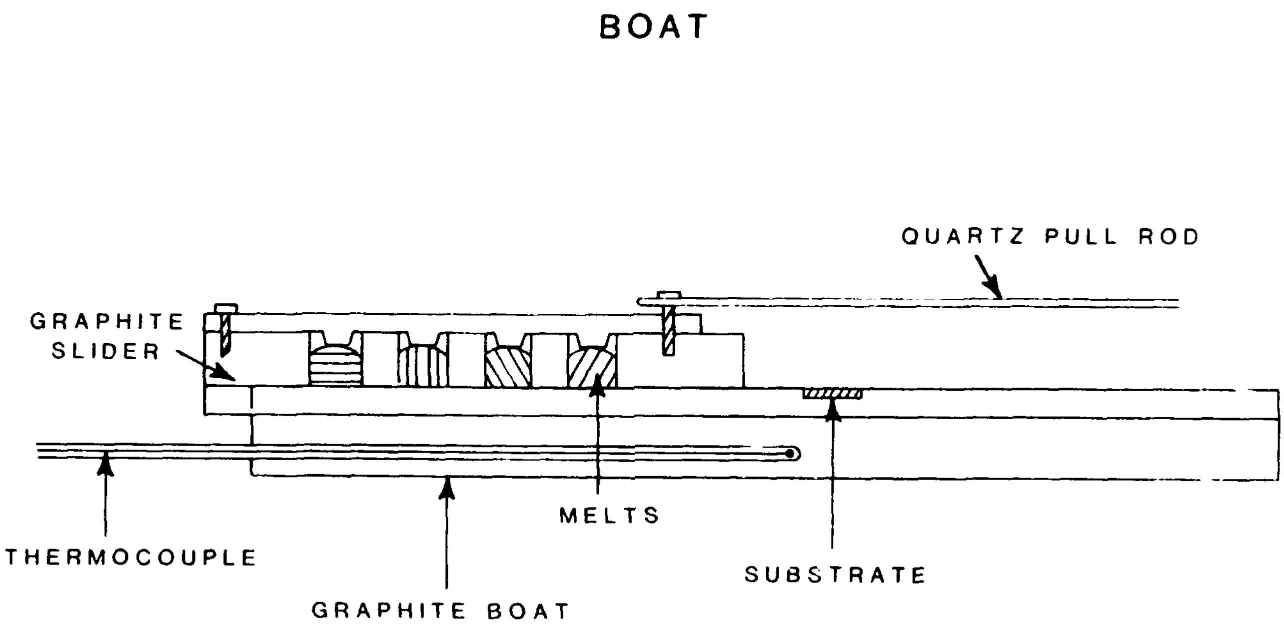

Figure 8. Sliding Method

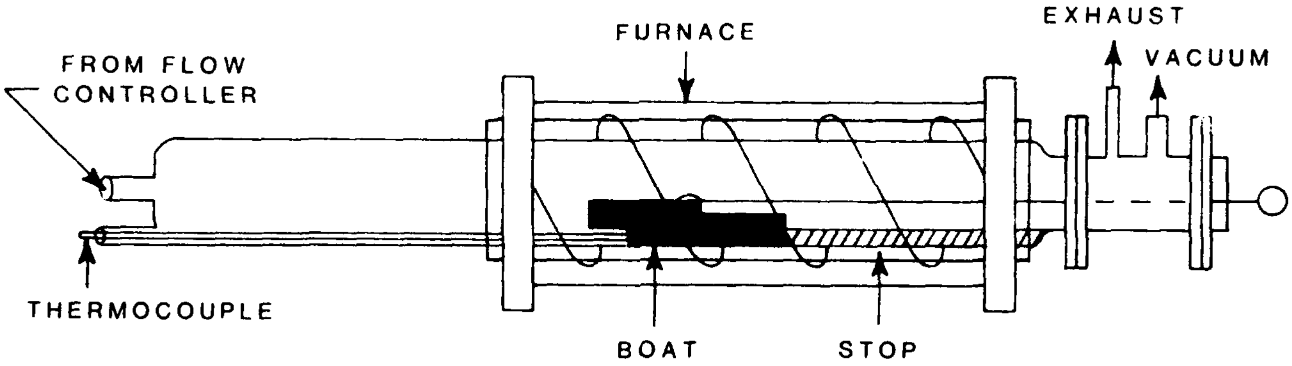

Figure 9. LPE System

Quartz is the material of choice because it can withstand high temperatures (quartz melts at 1600° C but is reduced in H_2 at 800° C), it can be obtained in high purities (reducing background contamination), and it is transparent (facilitating growth monitoring). The tube has one gas inlet. Gas flow is set, controlled, and monitored by mass flow controllers. Dry nitrogen is used to flush the system and keep a constant, pure ambient flow through the apparatus when not in use.

During a growth run, hydrogen is passed through the system. The highest possible gas purity is assured by passing the hydrogen through a palladium cell. Only atomic hydrogen will pass through the palladium, effectively screening out impurities. Hydrogen is used as the ambient because it acts as a reducing agent at growth temperatures, preventing native oxides on the surface from interfering with growth. We have installed flash arrestors on the exhaust line to prevent flashbacks or explosions. An in-line regulator limits the pressure entering the system to 5 psi, avoiding over-pressurization.

A small quartz tube containing a type K (chromel-alumel) thermocouple is inserted into a hole drilled into the bottom of the boat to measure the temperature directly under the substrate bin. A stainless steel outlet flange is connected to the large quartz tube by O-ring seal and incorporates the gas exhaust, a vacuum port, and a linear motion push-pull feedthrough used to position the melts over the substrate. A one-way check valve has been installed on the exhaust line. The check valve seals the system during evacuation and opens at 2 psi when backfilling. Exhaust line bubblers, partially filled with silicone diffusion pump oil, prevent back-streaming contamination.

A resistance furnace is mounted horizontally on Teflon rails so it can be positioned to obtain the proper thermal profile in the system. The furnace has low thermal mass so it can be heated or cooled rapidly. To quickly drop the temperature at the conclusion of a run, a small bank of fans has been installed. Time and temperature are set and monitored by a programmable temperature controller. Evacuation is performed by a rotary vane pump.

4. GROWTH MATERIALS

4.1 Substrates

All of our LPE growth has been on (100) indium phosphide (InP) substrates. We have achieved high-quality growth on semi-insulating (Fe-doped), undoped (n-type), and n^+ substrates. Wafers used for substrates must be highly polished and free of any scratches or residue left from the cleaning process. We begin with a standard 50 mm wafer, 350 μm thick, then dice it into 7.5 mm squares. The wafer is mounted face down on a vacuum chuck and scribed with a diamond tip. Mounting the wafers face down localizes damage created by scribing to the back of the substrate while the growth surface remains free of defects that may propagate into the epilayer. The wafer is scribed instead of cleaved because a sample with more exact dimensions can be obtained. However, cleaving results in less total damage to the substrate. This issue is addressed further in Section 10.2.

4.2 Melt Materials

Solvent material consists of 99.99999 percent pure (denoted hereafter as 7N), 5g indium slugs. Solute materials come from 5N pure, unintentionally-doped wafers (InP, GaAs, InAs) that have been cut up for this purpose. Polycrystal, as well as single crystal, wafers are suitable.

4.3 Dopants

Many researchers use Zn, Cd, Mn, or Mg for p-type dopants in the InP system.[5,6,7,8] We have chosen Mg as the p-type dopant because it has a small diffusion coefficient in the solid phase (movement of the dopant in the crystal lattice is small). Mg has a lower vapor pressure than Zn or Cd and a high distribution coefficient (weight ratio of solute concentration incorporated into the solid film to that present in the liquid melt). Using the calculations of Beneking,[9] we have been able to dope up to 5×10^{18} cm^{-3} by adding 1×10^{-4}g Mg in 5g In. We have not had problems with MgO forming in the melts or on the surface of the epitaxial layer as has been reported elsewhere.[10] Mg diffusion into the substrate during growth, as determined by differential Hall measurements, has been minimal. We use a 5N Mg ribbon as a source. The ribbon is etched back in 1M HNO_3 to remove surface contamination.

Sn, Te, and Ge are n-type dopants in the InP system. We have chosen to use Sn because it is readily available in high purities (5N) and easy to manipulate in the form of wire. Tin has a very low (0.0019) distribution coefficient;[11] as a result, 2 mg Sn must be added to 5g In to produce a 1×10^{18} cm^{-3} carrier concentration.

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[5] Takeda, Y., Kuzuhara, M., and Sasaki, A. (1980) *Jpn. J. Appl. Phys.*, **19**:899.

[6] Fujita, S., Matsuda, K., and Sasak., A. (1981) *Jpn. J. Appl. Phys.*, **20**:889.

[7] Fujita, S., Kuzuhara, M., Yagyu, M., and Sasaki, A. (1982) *Solid-State Electron.*, **25**:359.

[8] Tabatabaie-Alavi, K., Markunas, R., and Fonstad, C. (1979) **1979 Intern. Electron Devices Meeting**, (*IEEE*, New York).

[9] Beneking, H., Grote, N., and Selders, J. (1981) *J. Crystal Growth*, **54**:59.

[10] Takeda, Y., Kondo, M., and Sasaki, A. (1984) *J. Crystal Growth*, **66**:475.

[11] Astles, M., Smith, F., and Williams, E. (1973) *J. Electrochem. Soc.*, **120**:1750.

5. GROWTH RUN PREPARATION

5.1 Sample Cleaning

Proper cleaning of the substrate and melt materials is essential to insure high quality growth. Substrates must be free of both organic and inorganic contamination. Many different sample cleaning methods have been reported in the literature.[12,13] We have settled on the method outlined in Table 2.

Table 2. Cleaning Methods.

1. Degrease in organic solvents: trichloroethylene, acetone, methanol.
2. Etch for 5 sec. in 0.5 vol. percent bromine/isopropanol.
3. Rinse with methanol.
4. Etch oxide in HF for 1 minute (full strength, 5M).
5. Rinse with deionized water.
6. Dip in Methanol. Blow dry with nitrogen.

Although bromine evaporates faster in isopropanol, the etch is much smoother than bromine/methanol. Prolonged etching in HF will damage the InP surface. A prolonged dip in methanol will allow the surface to reoxidize.[14]

Substrates must be blown dry with nitrogen. Unintentional air drying of solvents on the surface will leave behind a growth-inhibiting film (Figure 10). Exposure to air after cleaning must be minimal to avoid organic contamination and minimize the growth of native oxides. The substrate is loaded into the boat within 1 min. of cleaning. Then the chamber is closed and evacuated to 10 millitorr, backfilled with hydrogen and flushed for one hour at room temperature.

5.2 Cover Piece

An InP cover piece is used to protect the substrate from thermal degradation. At growth temperatures (500-700° C), the vapor pressure of phosphorus is extremely high, causing

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[12] Guivarc'h, A., L'Haridon, H., and Pelous, G. (1984) *J. Appl. Phys.*, **55**:1139.

[13] Schmitt, F., and Susa, N. (1983) *Jpn. J. Appl. Phys.*, **22**:761.

[14] Knauer, A., Hirsch, D., Starke, R., and Zeimer, U. (1989) *Cryst. Res. Technol.*, **24**:443.

phosphorus to dissociate from the substrate surface quite rapidly, forming indium pits.[15] The damage shown in Figure 11 is typical. Unless the substrate is protected, the surface will be rendered useless in minutes. We have tried numerous approaches to avoid this condition. One general approach is the proximity method, in which a cover is placed in close contact with the InP surface to be protected. When the slider is pulled to position the melt over the substrate, the cover is pushed out of the way. Various cover materials have been tried, including graphite, GaAs, and InP.

Another approach is to place the substrate under a container of crushed InP. Crushed InP is contained in a small slot in the slider, above the substrate. Crushed InP provides a localized phosphorus overpressure, retarding phosphorus dissociation at the sample surface. Phosphine gas can also be used to provide a phosphorus overpressure in the system. However, phosphine is highly toxic and requires elaborate ventilation facilities.

To avoid the problem of surface decomposition, some researchers use a meltback technique.[16,17] Meltback is the dissolution of the top of the substrate in a phosphorus-deficient melt, effectively stripping back a few microns of substrate, thus removing the thermally damaged surface. We have found that this technique creates as many problems as it solves. Quite often, melt carry-over (indium residue) is left behind on the surface and around the edges of the substrate. When the growth solution is pulled over the substrate, the excess indium mixes in and changes the ratio of constituents. The thermal gradient across the melt affects the meltback rate. Etching is usually slower around the edge of the melt because it is cooler than the center. Therefore, meltback does not leave a uniform surface.

We have determined that the proximity approach, using a highly polished InP cover placed face down on the substrate, is simplest and most effective. The cover piece must be replaced periodically because it is subject to the same thermal degradation as the substrate. The cover piece tends to oxidize between runs and, as a result, must be dipped in HF before each run.

6. INDIUM PHOSPHIDE (InP)

6.1 InP Characteristics

Growing InP on InP has proven to be the most difficult in this system because of the volatility of phosphorus. InP growth is controlled by the diffusion of phosphorus in the melt and is a function of the amount of phosphorus supplied to the melt-substrate interface and the rate at which it is supplied. Although the diffusion constant of phosphorus increases with temperature, the vapor pressure of P over InP increases also, resulting in a greater amount of

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[15] Sartorius, B., Schlak, M., Rosenzweig, M., and Parschke, K. (1988) *J. Appl. Phys.*, **63**:4677.

[16] Stojanoff, V., Shahidi, M., McDevitt, T., and Mahajan, S. (1989) *Mater. Science and Engineering*, **B3**:279.

[17] Ohtsuka, K., Matsui, T., and Ogata, H. (1988) *J. Crystal Growth*, **87**:338.

dissociation. Because of the high diffusivity of phosphorus at temperatures above 700° C (2.5 $cm^2 s^{-1}$ at 750° C),[18] InP grows faster and has smooth surface morphology. However, the surface degrades rapidly when growth is terminated. As phosphorus diffusion slows at temperatures below 700° C (0.5 $cm^2 s^{-1}$ at 625° C), InP grows slower and surface morphology is consistently wavy, but dissociation problems are less pronounced. It is possible that as growth temperature decreases, phosphorus atoms are locked in place faster and lack the thermal energy necessary to leave the lattice if they have frozen in the improper site.

6.2 Melt Preparation

Prior to melt preparation, the source substrate is cleaned as previously described. The substrate is placed in the boat along with an indium slug that has been taken directly from the supplier's packaging. Indium phosphide melts are prepared by placing the pure indium melt over the InP source substrate for 12 hr. at a temperature slightly above the desired growth temperature. InP dissolves until the indium solvent is saturated. After the melt is saturated, it is pushed off the source and the source is removed from the boat. If the growth temperature is above 600° C, a two-phase melt is used. A two-phase melt is prepared in the same way as the melt previously described but, an additional InP piece is placed on top of the melt, held there by surface tension. The additional solid-phase piece serves as a semi-infinite source of phosphorus to replace the phosphorus escaping from the melt at high temperatures. The additional solid piece also serves as a second nucleation point, reducing diffusion to, and nucleation on, the substrate. If the growth temperature is below 600° C, a single-phase melt is used. At lower temperatures the phosphorus depletion problem is not as acute so a replenishing source is not necessary. Because the diffusion of phosphorus through the melt is small in this temperature regime, the substrate must serve as the only nucleation site.

6.3 InP Growth

Supercooling, describing previously, is the preferred cooling method. After the melt is heated well above the growth temperature and held long enough to homogenize (approximately 1/2 hour), it is cooled to form a supersaturated solution.

Table 3 gives the time/temperature parameters of a typical growth run for a melt prepared to come into equilibrium at 625° C.

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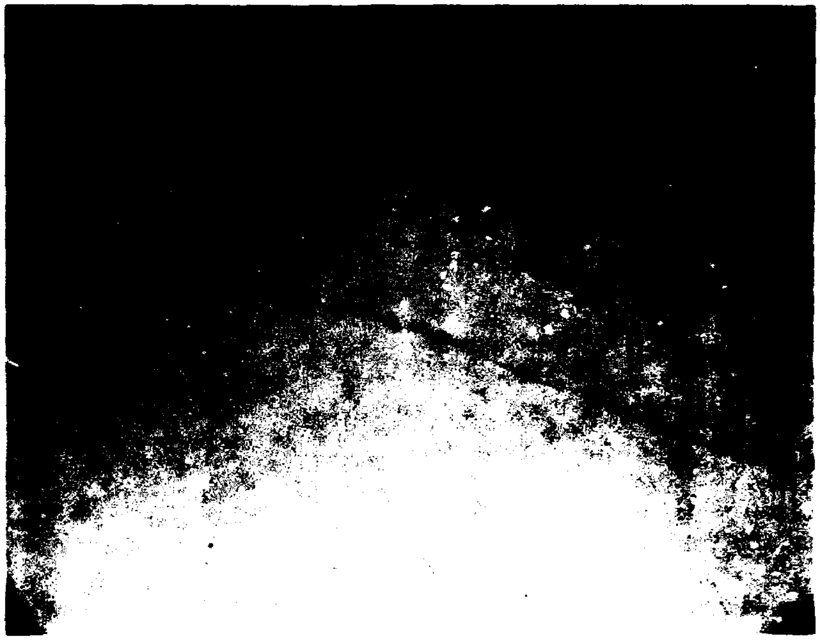
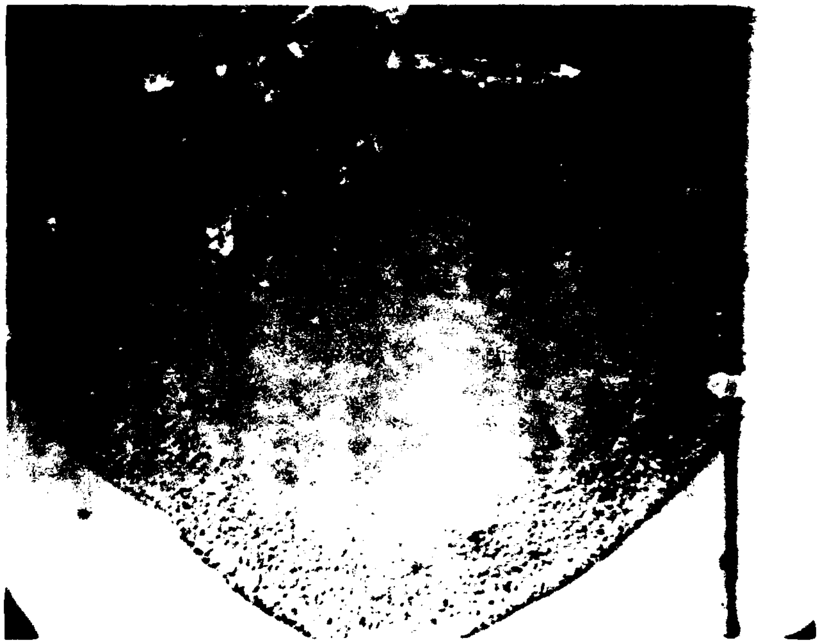
[18] Stojanoff, V., Shahidi, M., McDevitt, T., and Mahajan, S. (1989) *Mater. Science and Engineering*, **B3**:279.

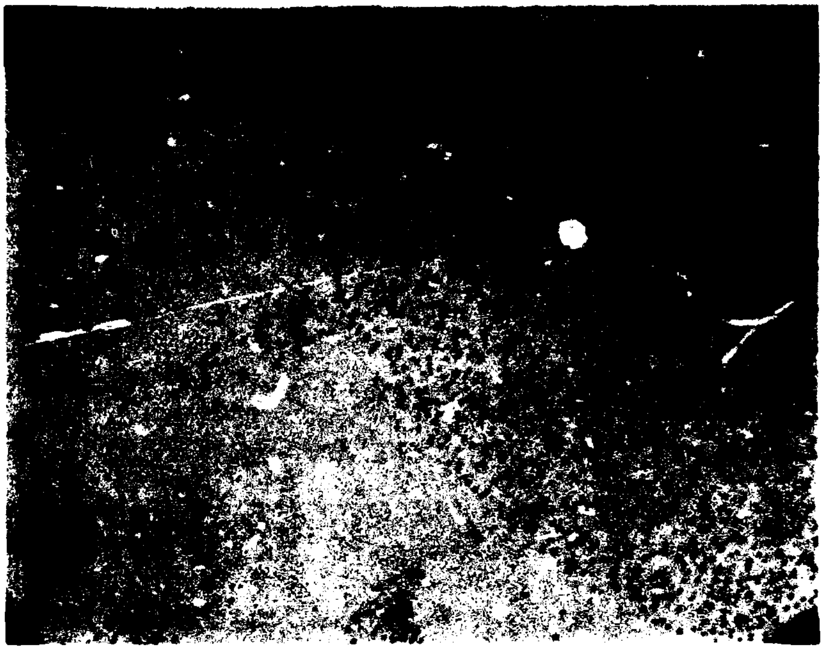


LPE #45 160X

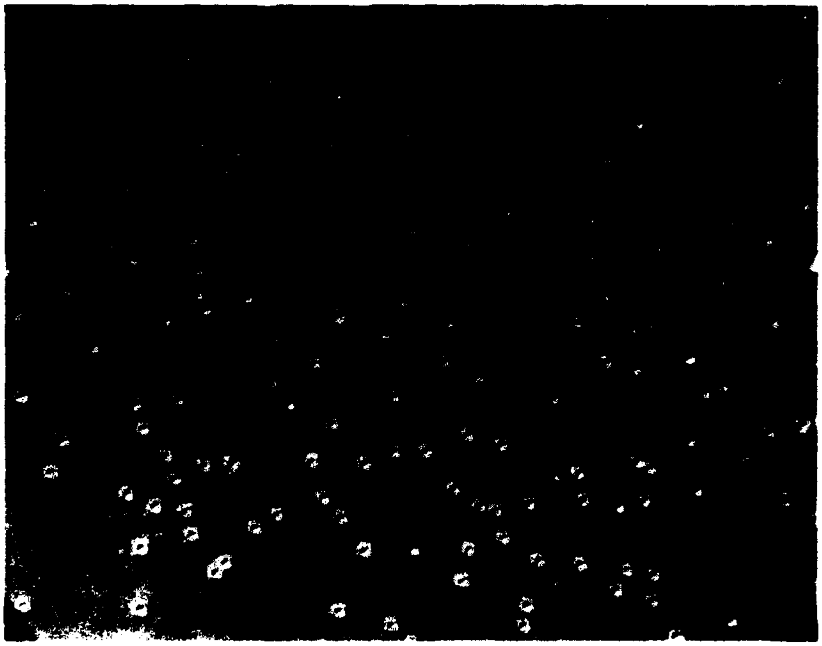


LPE #45 800X

Figure 10. Residue From Cleaning Process



LPE #45 16X InP / InP



LPE #45 800X InP / InP

Figure 11. Thermal Damage due to Phosphorus Loss

Table 3. InP Time/Temperature Parameters.

1. 30 min. to 675° C
2. 30 min. at 675° C
3. 10 min. to 630° C
4. 10 min. at 630° C
5. 60 min. to 600° C

The melt is brought up to temperature and homogenized (steps 1 and 2), then ramped down and stabilized close to equilibrium (steps 3 and 4). A constant cooling rate is established in step 5. Growth is initiated at 624° C with 1 degree of supercooling. InP nucleates in small islands and spreads more rapidly in the lateral direction, around the islands, than in the vertical direction, as shown in Figure 12. At 700° C the growth rate is 0.3 μm per minute (cooling rate - 0.25 deg/min). At 625° C the average growth rate falls to 0.25 μm/min for a number of different cooling rates (0.25 to 2 deg/min). At 550° C the growth rate drops rapidly to 0.1 μm/min (cooling rate - 1 deg/min). This change of growth rate is characteristic of diffusion-controlled epitaxial depositions. The growth rate drops slightly when the melt is used repeatedly. A melt is typically used for 5 to 10 runs.

We have grown p^+–InP using Mg as a dopant and n^+–InP using Sn as a dopant. No special procedures are required other than to bake the melts for 2-3 hours at temperatures 20 to 50° C above the growth temperature to thoroughly mix the constituents.

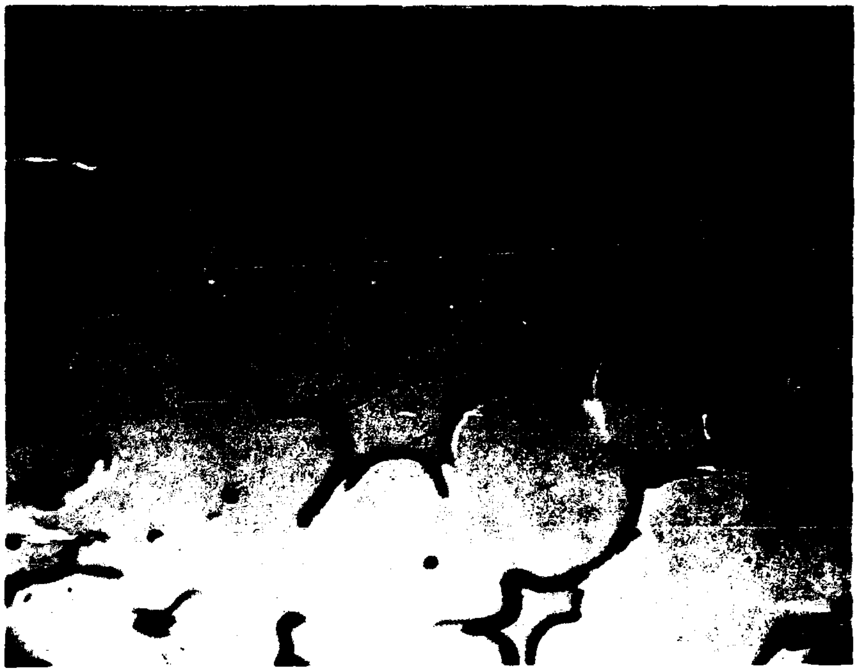
7. INDIUM GALLIUM ARSENIDE (InGaAs)

7.1 InGaAs Characteristics

We are interested in indium gallium arsenide because its small bandgap (0.749 eV), and high speed characterisics (mobility > 11,000 $cm^2\ V^{-1}\ s^{-1}$ at 300K) are attractive for use in photodetectors. InGaAs has proven to be the least difficult material to grow in this system. It is not limited by diffusion of Ga and As in the melt. Surface morphology can be highly specular.

InP ON InP

LPE #44 80X



LPE #60 160X

Figure 12. Island Growth.

7.2 Melt Preparation

An InGaAs melt is more difficult to make than an InP melt. The constituents must be carefully measured since InGaAs is lattice matched to InP only with an $In_{.53}$ to $Ga_{.47}$ solid ratio. Although atomic fractions of the constituents in solid phase must remain constant atomic fractions of the constituents in liquid phase must be varied for different growth temperatures because distribution and diffusion coefficients change with temperature. These fractions can be found in the literature.[19] We generally grow at 620° C with the atomic fractions shown in Table 4.

Table 4. InGaAs Liquidus Atomic Fractions.

X_l (Ga) - 0.0210
X_l (As) - 0.0458
X_l (In) - 0.9332

The source of indium is a high purity, 5g indium slug. The Ga and As come from undoped wafers of GaAs and InAs. To determine the amount of solid material needed to compose the properly proportioned melt, the equations in Table 5 must be used.

Table 5. Equations for Melt Constituents.

$$m_{GaAs} = \frac{M_{GaAs}}{M_{In}} \bullet \frac{X^l_{Ga}}{X^l_{In} + X^l_{Ga} - X^l_{As} - X^l_{P}} \bullet m_{In}$$

$$m_{InAs} = \left[\frac{M_{InAs}}{M_{GaAs}} \frac{X^l_{As} - X^l_{Ga}}{X^l_{Ga}}\right] m_{GaAs} m_{InAs} = \left[\frac{M_{InAs}}{M_{GaAs}} \frac{X^l_{As} - X^l_{Ga}}{X^l_{Ga}}\right] m_{GaAs}$$

$$m_{InP} = \frac{M_{InP}}{M_{In}} \frac{X^l_{P}}{X^l_{In} + X^l_{Ga} - X^l_{As} - X^l_{P}} m_{In}$$

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[19] Hseih, J. (1981) *IEEE J. Quantum Electron.*, **QE-17**:118.

The constituents are placed together in a single bin in the boat. They must be baked overnight at 25° C above the equilibrium temperature to ensure thorough mixing.

7.3 InGaAs Growth

During an actual InGaAs growth run, the same time and temperature parameters are used as for InP growth (Table 3). Growth is initiated at 620° C. The growth rate for InGaAs is 1.5 µm/min, much faster than for InP. We have found that the growth rate of InGaAs increases to 3.9 µm/min when the melt is baked out for 24 hours at temperatures above 700° C. (The melts are baked at elevated temperatures to reduce contamination, resulting in a lower background carrier concentration.) One possible explanation for this phenomenon is that as unwanted impurities are driven out of the melt, the diffusivity of the remaining constituents is increased. As a result, the growth becomes limited by rate of reaction, not by rate of diffusion. It has been reported that a carrier concentration as low as 1×10^{15} cm^{-3} is obtainable with these procedures.[20,21] We have achieved 5×10^{15} cm^{-3} in our system. We feel the lower doping levels can be reached with some redesign and stringent attention to cleanliness. We have grown p^+ layers (Mg doped) and n^+ layers (Sn doped) for use in fabricating photodetectors.

8. INDIUM GALLIUM ARSENIDE PHOSPHIDE (InGaAsP)

8.1 InGaAsP Characteristics

Whereas the ternary $In_{.53}Ga_{.47}As$ is lattice matched to InP at only one solid composition, the quaternary InGaAsP can be lattice matched over a wide range of compositions. Not only can the In to Ga ratio be varied, but the As to P ratio can be varied as well. Different compositions will result in growth of material with different bandgaps (0.75 to 1.35 eV) and thus different emission or absorption spectra (0.92 to 1.55 µm). As a result of the wide range of lattice matching conditions, devices can be tailored to meet particular requirements. InGaAsP is used extensively for making laser diodes. This material is particularly attractive for use in LPE because it will not dissolve when InP is grown on top of it.

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[20] Ohtsuka, K., Ohishi, T., Abe, Y., Sugimoto, H., Matsui, T., and Ogata, H. (1988) *J. Crystal Growth*, **89**:391.

[21] Battacharya, P., and Rao, M. (1983) *J. Appl. Phys.*, **54**:5096.

8.2 Melt Preparation

We have been interested in material that will emit at the 1.3 μm wavelength (0.95 eV bandgap) and have focused on the $In_{.53}Ga_{.47}As_{.63}P_{.37}$ solidus composition. We generally grow at 635° C with the atomic fractions of constituents in liquid phase shown in Table 6.

Table 6. InGaAsP Liquidus Atomic Fractions.

X_l (In) -	0.9413
X_l (Ga) -	0.0107
X_l (As) -	0.0480
X_l (P) -	0.0017

A complete table with the different solidus and liquidus information has been compiled by M.A. Pollack.[22] An InGaAsP melt is prepared in much the same manner as an InGaAs melt. The source of the indium is a high purity (7N), 5g indium slug. The Ga and As come from undoped wafers of GaAs and InAs. To determine the correct amount of material to add, the same equations as those used in the InGaAs system must be used. (See Table 5). The phosphorus can be added in two ways. Using the standard equations, an exact amount of InP cut from a wafer can be added. The easier method is to place a small InP piece, in excess of the amount to saturate an InGaAs melt, on top of the melt as in two-phase InP growth. This method eliminates the need for exact measurements and provides a source of phosphorus as the melt becomes depleted.

8.3 InGaAsP Growth

InGaAsP is grown by step cooling. The temperature is dropped 2° C from the equilibrium temperature and held constant when growth is initiated. This method was employed because it produced the best surface morphology. The supercooling method produced the series of lines seen in Figure 13. Figure 14 shows the result of using the step cool method. The growth rate is 0.81 μm, faster than InP but slower than InGaAs. We can conclude that the diffusion coefficients of As and Ga are higher in In than the diffusion coefficient of P. As a result, the ternary and quaternary grow faster because the constituents are more readily supplied to the substrate/melt interface by the melt.

We have doped InGaAsP p-type for use in solid state laser fabrication. Once again, Mg was the dopant of choice.

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[22] Pollack, M., Nahory, R., DeWinter, J., and Ballman, A. (1978) *Appl. Phys. Lett.*, **33**:314.

9. CHARACTERIZATION

9.1 Hall/van der Pauw Measurements

Hall/van der Pauw measurements are used to determine net carrier concentration and mobility in bulk material or thin films. We have used this method to determine the effects of long, high-temperature bakeouts on carrier concentration and mobility in InP and InGaAs growth. Using Hall analysis we have determined that the carrier concentration falls and mobility rises when the growth materials are baked out (Figures 15 and 16). Unwanted impurities are driven out of the melt in prolonged, high-temperature bakeouts, reducing electrically active carriers and scattering centers. Occasionally we determine the distribution of electrically active carriers and carrier mobility through the entire layer (as opposed to a bulk measurement) with the anodization/etch method described by J.P. Lorenzo et al.[23] This method accurately determines the distribution of impurity dopants in the grown material. We have performed 77K Hall measurements in characterization of undoped InGaAs layers. At room temperature, mobility is affected by impurity scattering, lattice phonons, and carrier/carrier interaction. At 77K, the phonon interaction is minimized and a more accurate characterization of the carriers can be obtained.

9.2 X-ray Diffraction

To determine if the LPE layers are lattice matched, single-crystal and double-crystal x-ray diffraction measurements have been made. Rocking curves are (400) reflections with intensity (counts/sec) plotted vs relative diffraction angle (arc-seconds). The sharpness of the peak is a function of crystalline perfection. The magnitude of the peak is a function of crystal thickness. In our analysis the sharper peak is assumed to be due to the InP substrate and the remaining smaller and broader peaks due to the epilayers. This analysis shows that lattice matching of InGaAs to InP is outstanding (Figure 17). A lattice mismatch below 1000 parts per million (ppm) is considered adequate for device fabrication. Figure 17 shows that our material has a full width half maximum of 13 sec. and a mismatch of 130 ppm. The InGaAsP (shown in Figure 18) is slightly more mismatched at 660 ppm. The peak is less intense and broader, probably due a small amount of compositional grading in the film. As phosphorus vaporizes at the InP surface, small indium pits are left behind. Growth of InGaAsP on this roughened surface will produce local variations in composition because the indium/gallium ratio has been distorted. Composition variations are more critical to InGaAsP growth than to InGaAs growth because small compositional changes can lead to large changes in bandgap and emission wavelength.

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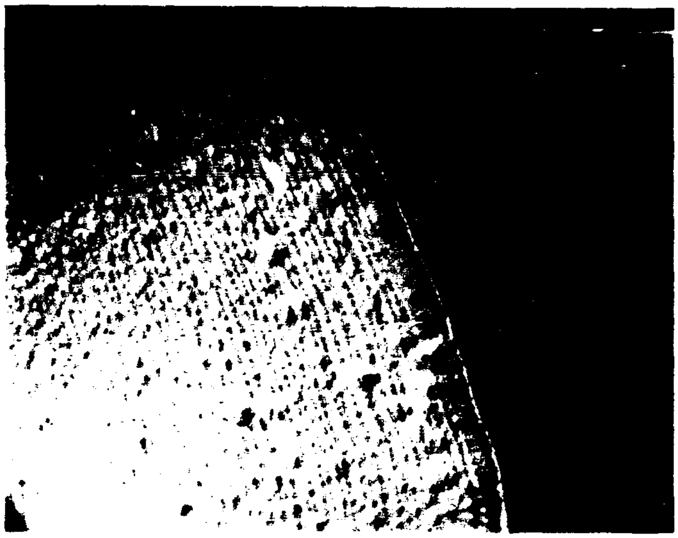
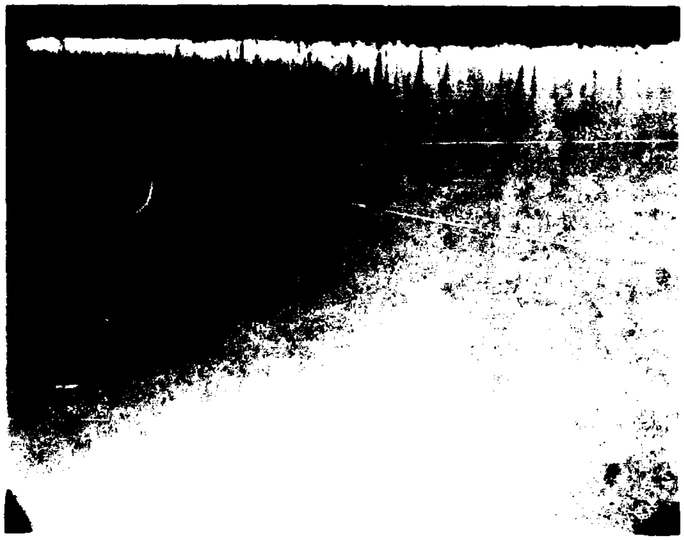
[23] Lorenzo, J., Davies, D., and Ryan, T. (1979) *J. Electrochem. Soc.*, **126**:118.



LPE #162 40X

Figure 13. InGaAsP Growth Supercooling

STEP - COOL



LPE #166 80X

Figure 14. InGaAsP Growth Step cooling

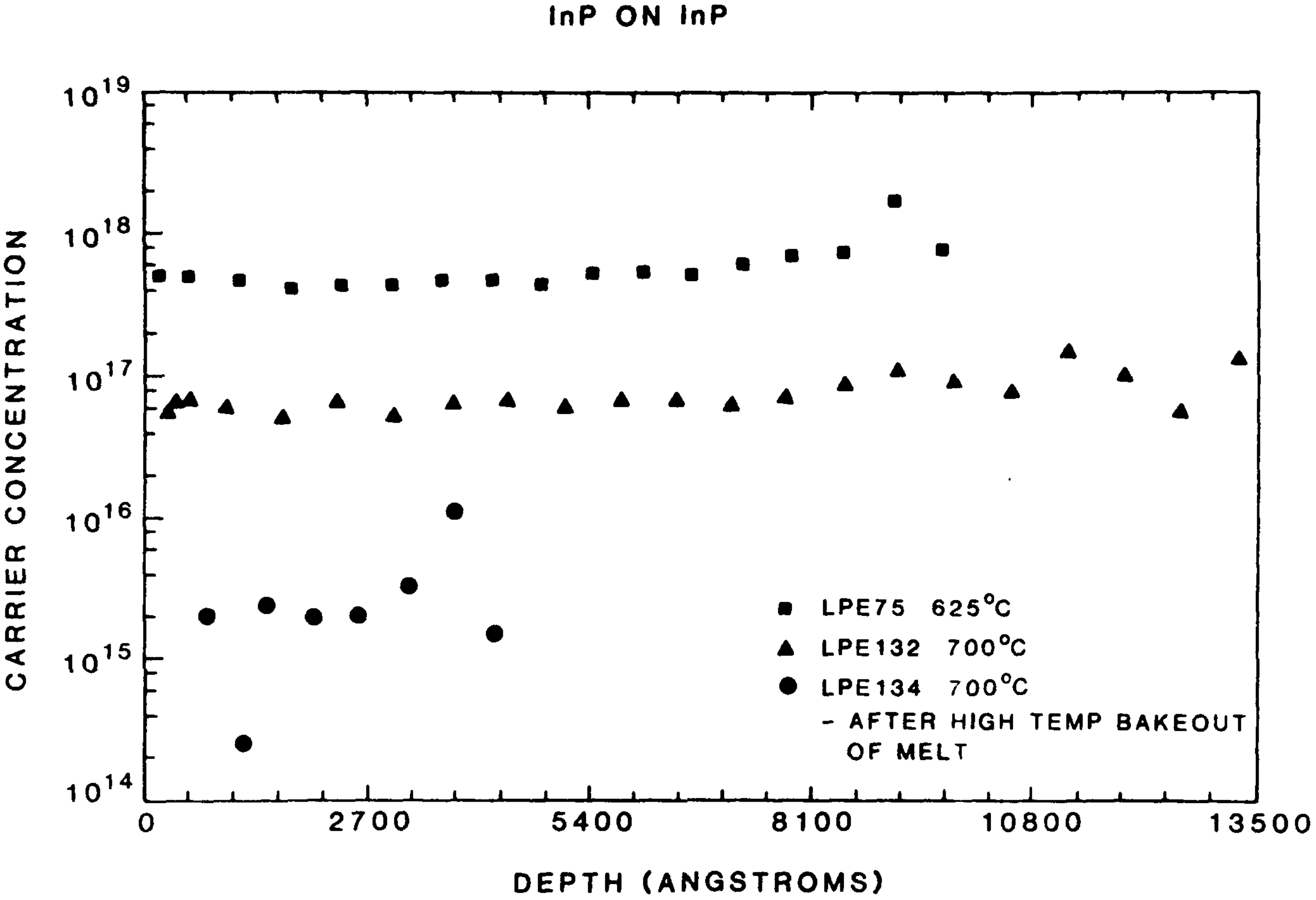


Figure 15. Carrier Concentration vs Depth

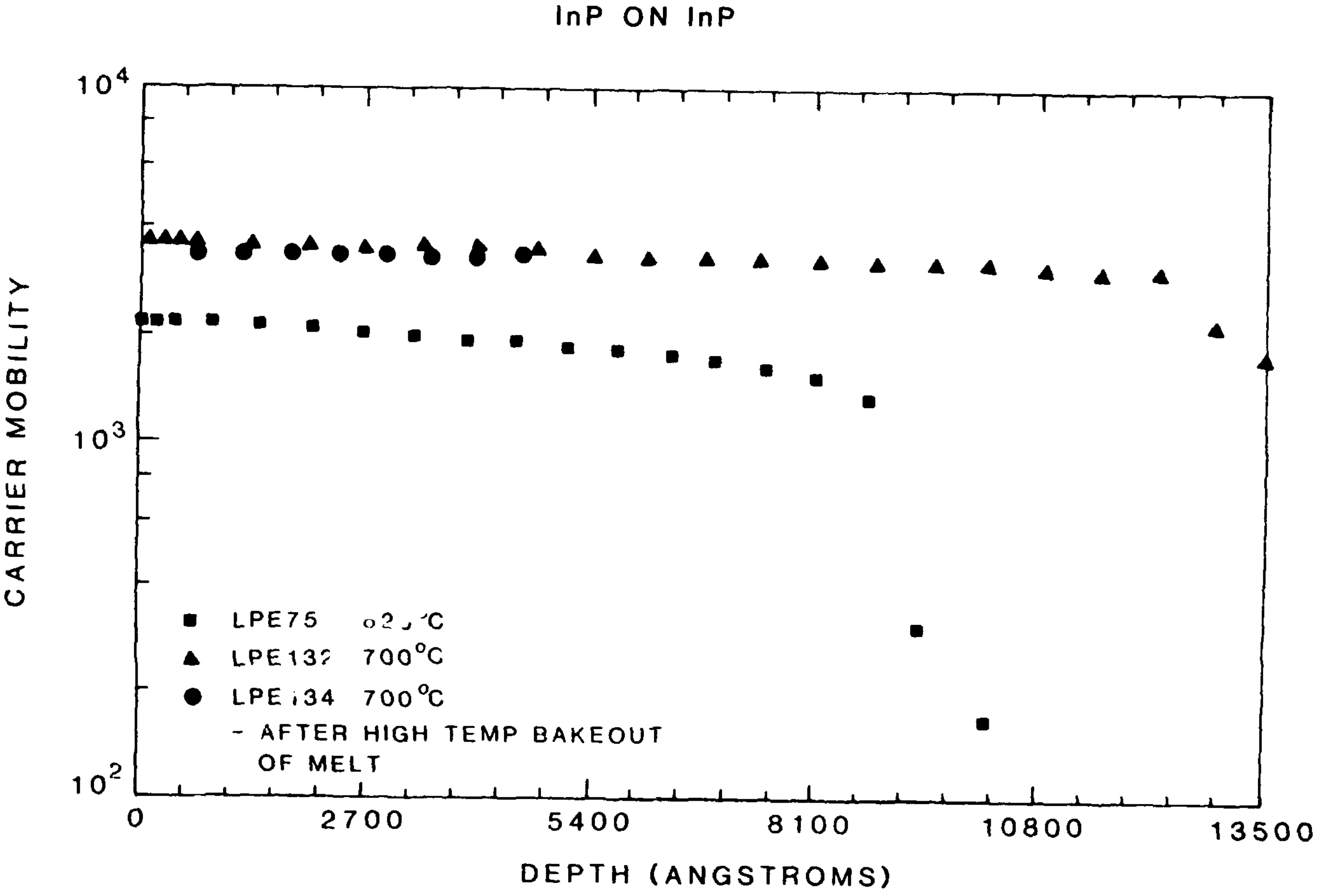


Figure 16. Carrier Mobility vs Depth

9.3 Photoluminescence

We have measured the photoluminescence (PL) of the InGaAsP material to ensure that its composition was correct and that it would emit at 1.3 µm. Photoluminescence is the optical radiation resulting from electronic excitation of a material by optical radiation (laser). Emission peaks will be at a wavelength corresponding to the bandgap of the material. A photodetector captures the emission as a monochrometer sweeps through a range of wavelengths. As was discussed earlier, small deviations in material composition will lead to significant changes in the bandgap of the epilayer. Photoluminescence curves plot intensity vs wavelength (Figures 19-21). Photoluminescence is sometimes performed at 77K and 4K. At these temperatures, emission peaks become narrower and more intense due to reduced phonon interaction.

In addition to determining the bandgap of a sample, photoluminescence will indirectly measure the impurities incorporated into the epilayer. Impurities will emit photons at wavelengths different from the wavelength of the host crystal, thus broadening the response peak. As a result, impurity concentration can be qualitatively determined by peak width.

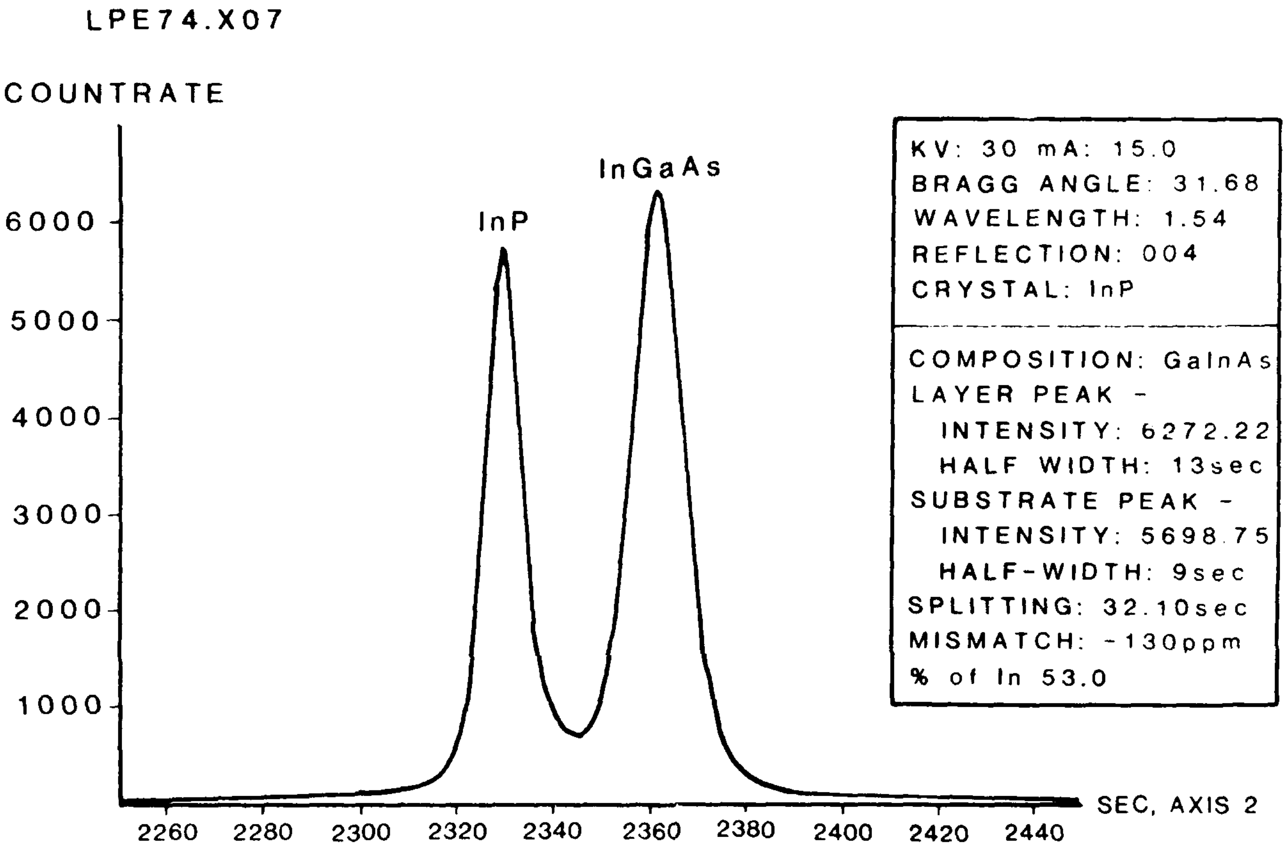
9.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is most useful at times when optical microscopy cannot provide the necessary magnification and depth of field. We have used SEM to look at the interface between the substrate and epilayer and between epilayers (Figure 22). Because growth by LPE is not completely uniform in thickness, SEM can provide a more accurate picture of layer thickness than a profilometer.

10. PERIPHERAL TOPICS

10.1 Device Issues

In an attempt to grow heterostructures, we found that InP will grow quite rapidly on InGaAsP at 550° C, but will not grow on InGaAs at any temperature. The InP melt will etch back the InGaAs layer. We have achieved limited success in developing a heterostructure photodetector. We decided to make a p-i-n structure. An intrinsic InGaAs layer was grown on an n^+ substrate. Subsequently, a p^+–InGaAs layer was grown on the intrinsic layer. After evaporating Au/Mg contacts, the sample was cleaved and mounted on a probe station.



KV: 30 mA: 15.0
BRAGG ANGLE: 31.68
WAVELENGTH: 1.54
REFLECTION: 004
CRYSTAL: InP

COMPOSITION: GaInAs
LAYER PEAK -
INTENSITY: 6272.22
HALF WIDTH: 13sec
SUBSTRATE PEAK -
INTENSITY: 5698.75
HALF-WIDTH: 9sec
SPLITTING: 32.10sec
MISMATCH: -130ppm
% of In 53.0

Figure 17. X-ray Diffraction-InGaAs

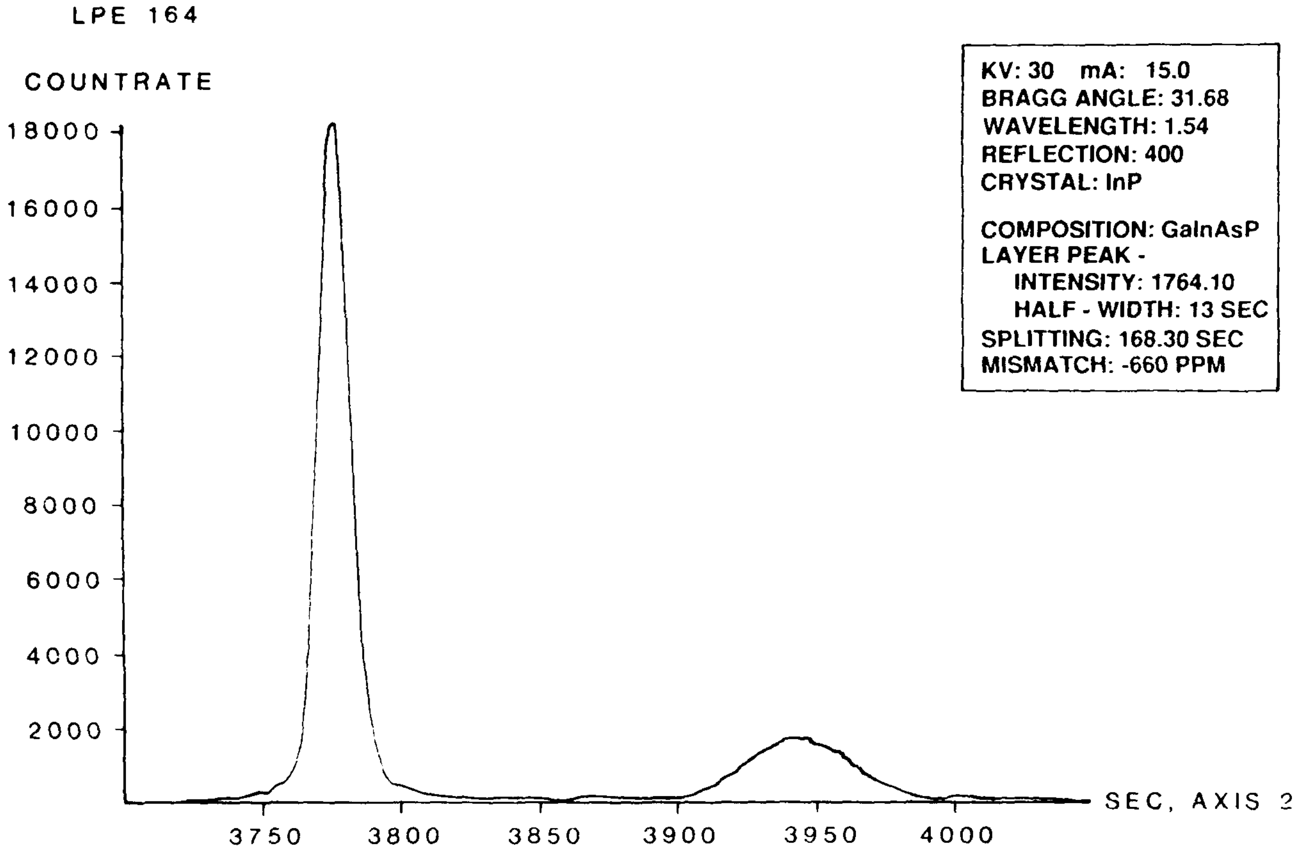


Figure 18. X-ray Diffraction-InGaAsP

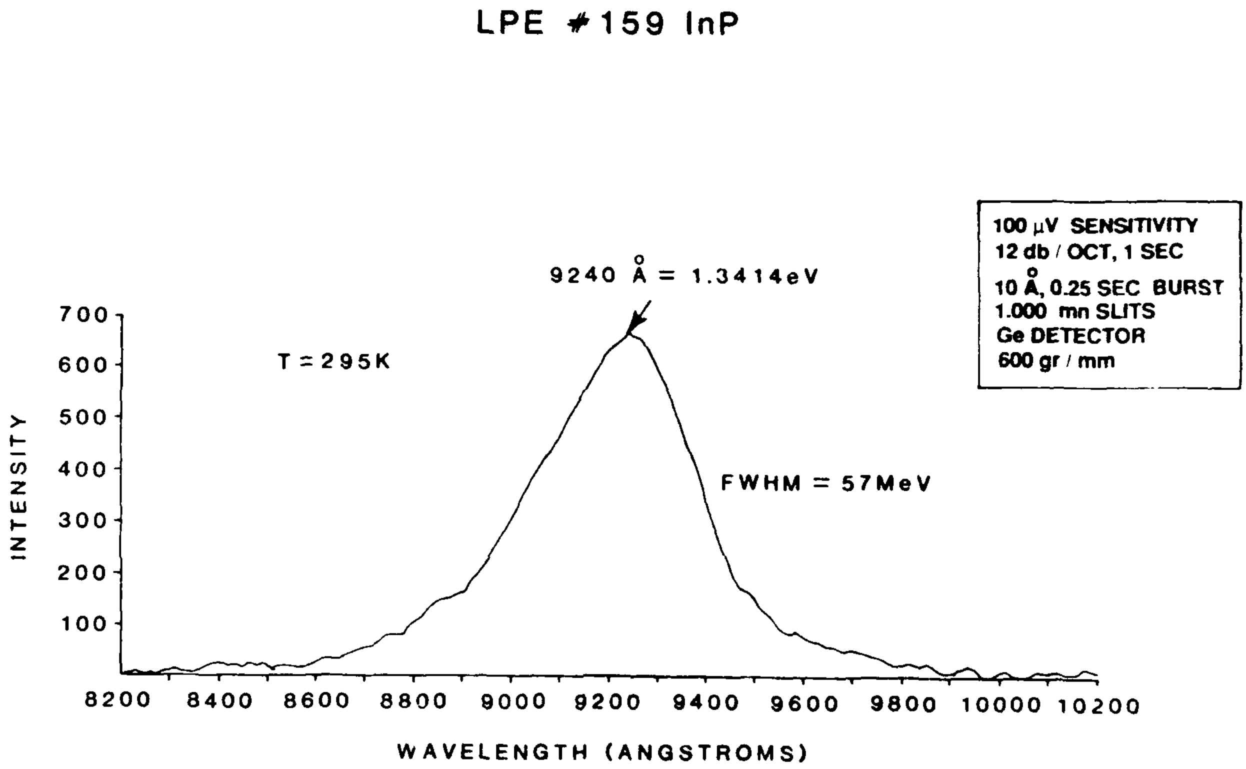


Figure 19. Photoluminescence Plot-InP

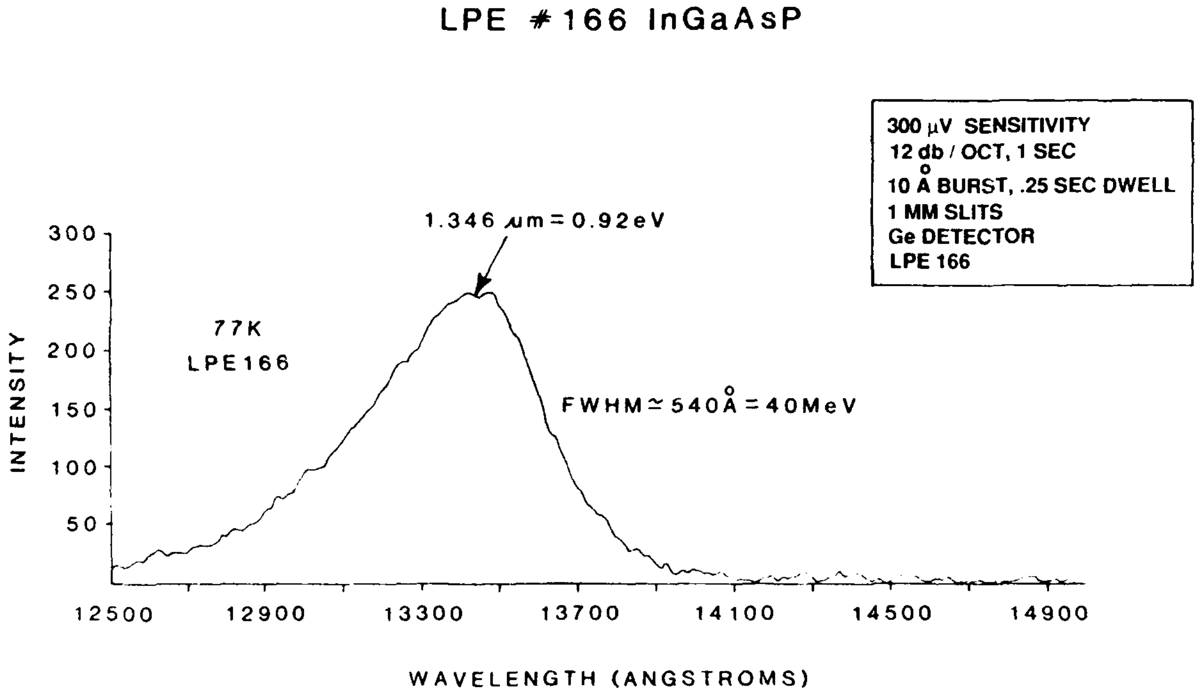


Figure 20. Photoluminescence Plot-InGaAsP

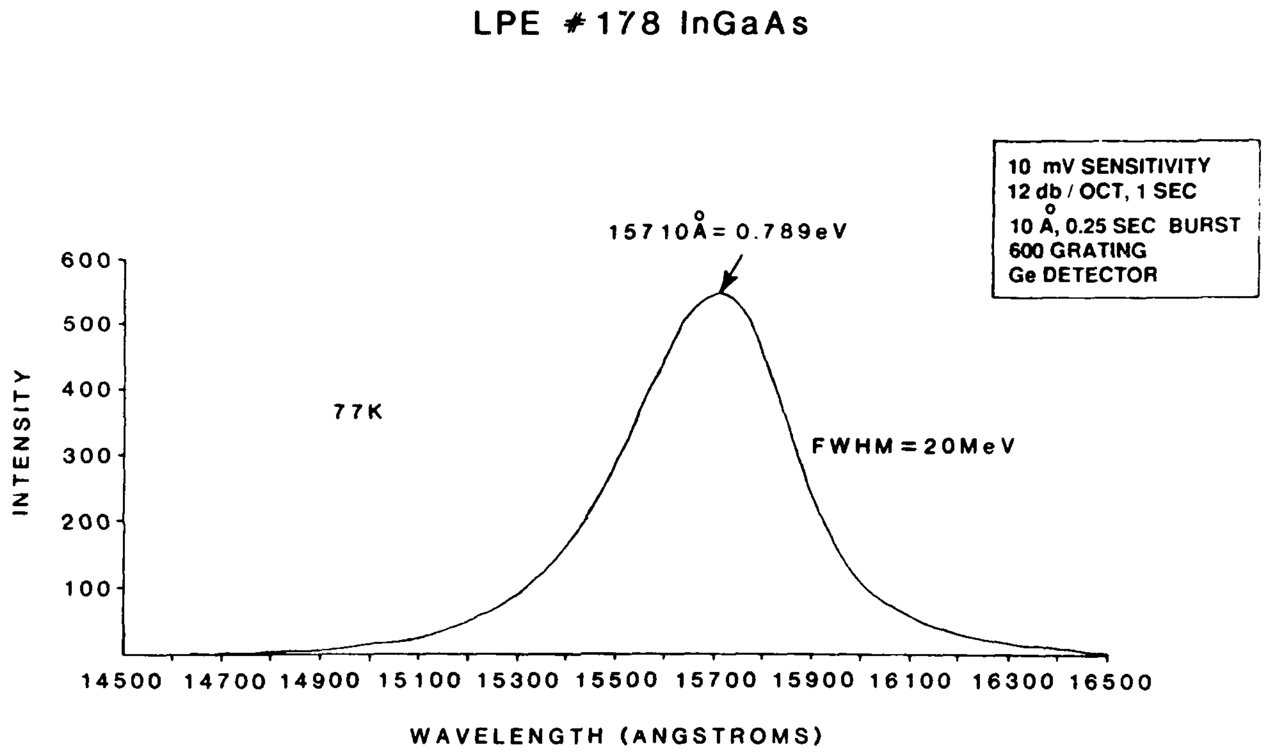


Figure 21. Photoluminescence Plot-InGaAs

The first samples were leaky and had small response. To reduce the series resistance of the substrate, the sample were thinned to 1.75 mm. A thin silicon dioxide film was deposited on the surface for passivation. These techniques improved the response and reduced the turn-on voltage to 1 V. The breakdown voltage was −25 V.

We have fabricated a solid state laser using LPE. The design was a simple double heterostructure. A p^+–InGaAsP layer was grown on an n^+–InP substrate. Subsequently a p^+–InP layer was grown on the InGaAsP. The epitaxial growth was fine, but the processing proved to be difficult. We had difficulty cleaving a piece small enough to be effective. Cleaving, mounting, contacting and passivating must be done with great care to obtain reasonable emission.

10.2 Cleaving vs Scribing

We have conducted a small study on the effects of cleaving versus scribing on substrates and epilayers. Cleaving is the splitting of a sample along crystal planes. Cleaving is relatively simple for samples with (100) orientation. A small downward force applied with the corner of a razor blade, perpendicular to a side, is sufficient to cleave the sample. Scribing is the scratching of a line across the surface to strain the sample where the break should occur. InP will break along the scratched lines when tapped, much like a piece of glass. Wafers can be cut more precisely with a scribe, but as Figures 23 and 24 show, damage to the material is substantial compared to cleaving. Density and penetration of the damage is extensive, extending both perpendicular and parallel to the surface. These effects are critical in device fabrication. The leakage current of a photodetector is greater on a device that has been mechanically scribed. The epilayers are chipped on the edges and short circuits tend to be formed across the pn junction.

10.3 Melt Carry-over

One of the biggest disadvantages of LPE is the inability to completely wipe the melt off the wafer surface on termination of growth. Little pockets of melt remain behind on the surface and around the edges. This effect is called melt carry-over. Melt carry-over can be minimized by pulling the melt off the substrate as rapidly as possible upon termination of growth, maintaining a distance of no more than 75 μm between the top of the substrate and the bottom of the slider, and minimizing melt height.[24]

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[24] Wilson, R., Besomi, P., and Nelson, R. (1985) *J. Electrochem. Soc.*, **132**:172.

If a large amount of indium is left on the surface of InP or InGaAsP, nitric acid will etch it off. Mercuric chloride is a standard etchant for indium as well. Nitric acid will also selectively etch InGaAs very rapidly. Iodic acid or bromine/methanol will etch InP.[25,26]

11. CONCLUDING REMARKS

We have pursued the development of indium phosphide technology in support of the Air Force photonics initiative with the goal of improving and expanding command, control, and communication systems. The indium phosphide system (InP, InGaAs, and InGaAsP) is well suited for electro-optic, high-speed, high-power devices. The capability to grow epitaxial thin films is essential for device fabrication. We have developed a system for liquid phase epitaxial growth. Simplicity and cost effectiveness provide the impetus for developing this system. Although LPE has certain limitations, device-quality material can be obtained, equal to or better than thin films produced by other methods. Each thin film (InP, InGaAs, InGaAsP) has unique growth characteristics and requires different preparations and combinations of growth parameters. Proper characterization of the epilayers is necessary to determine if the material is within specifications. As with any new technology, a trial-and-error approach must be taken toward development. We have offered some procedures that have given us a measure of success in epitaxial growth and device fabrication.

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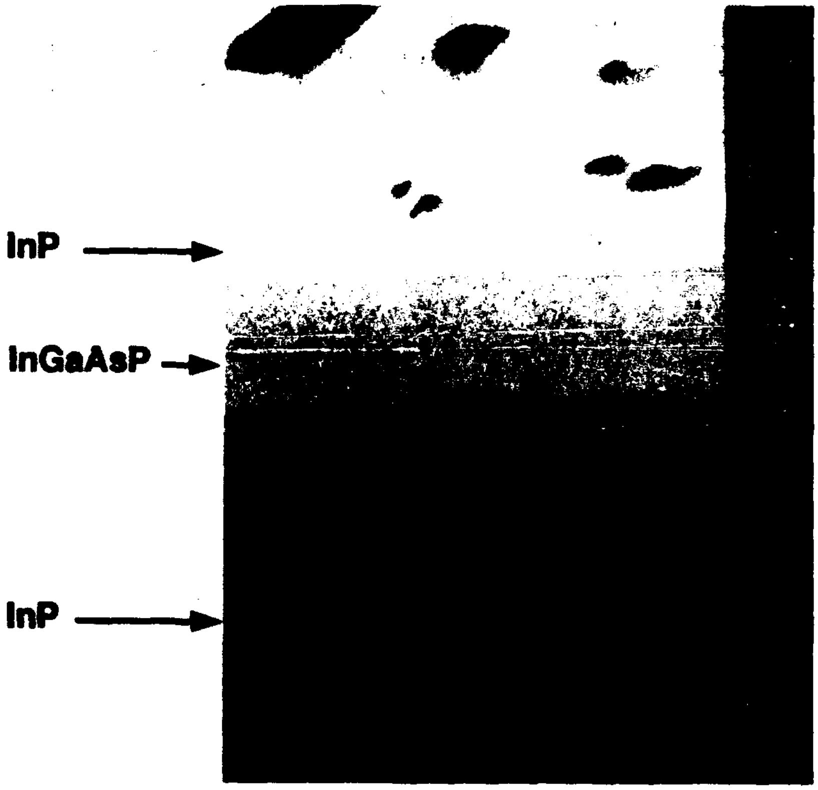
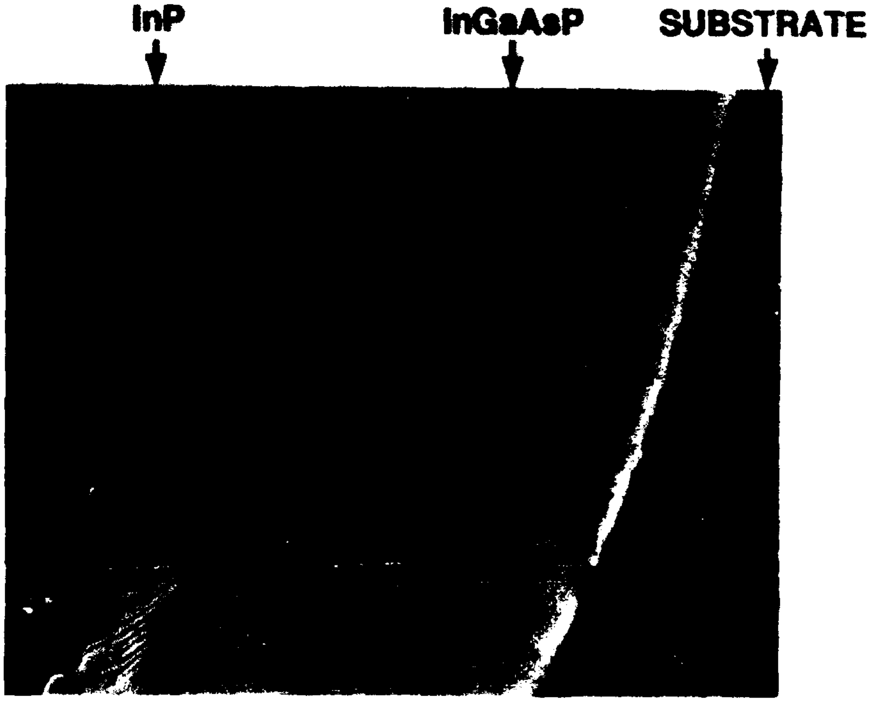
[25] Aspnes, D., and Studna, A. (1981) *Appl. Phys. Lett.*, **39**:316.

[26] Clawson, A., Collins, D., Elder, D., and Monroe, J. (1978) *Technical Note 592*, (NRL, San Diego).

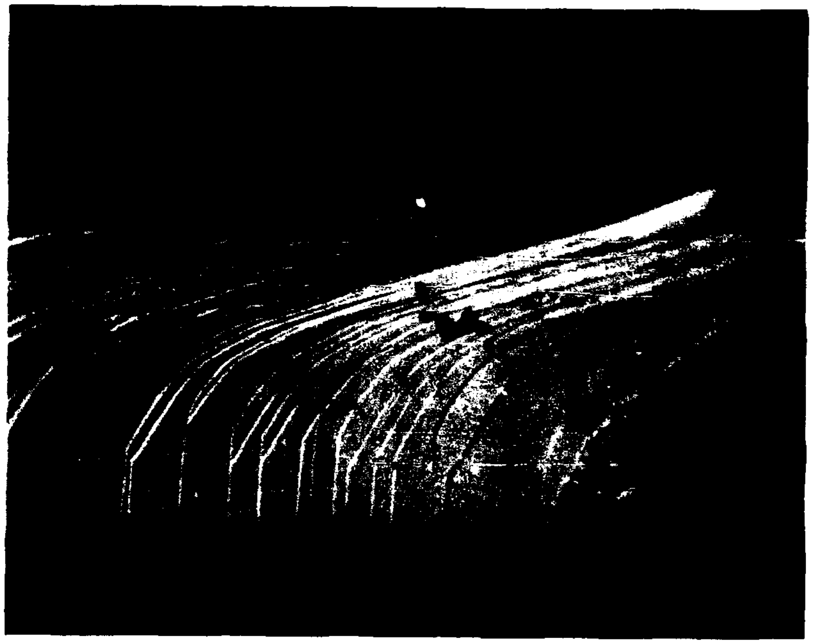


LPE #167 SEM



LPE #167 OPTICAL

Figure 22. Substrate/Epilayer Interface by SEM



LPE #39

LPE #39

Figure 23. Damage Produced by Cleaving

LPE #39

LPE #39

Figure 24. Damage Produced by Scribing

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