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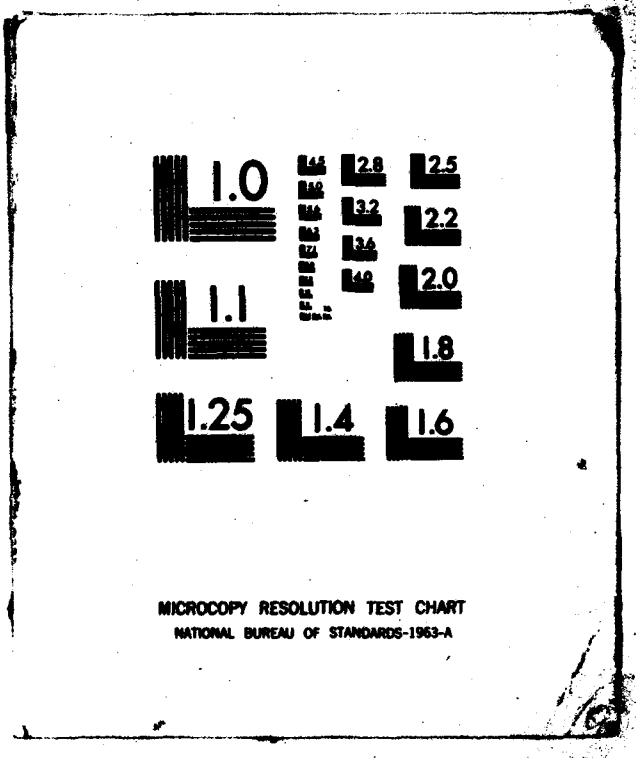
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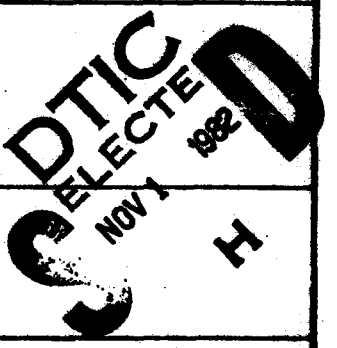

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Indium Phosphide MBE layers have been grown using a number of different phosphorus sources. Sources that produce a significant flux of P_2 or atomic phosphorus yield much higher quality epitaxial films than sources which are predominantly P_4. The best materials grown to date had room temperature mobilities greater than 3700 $cm^2/V \cdot s$ and were grown using a small [illegible]

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phosphorus source. The geometry of the IR phosphorus source is important. An incorrect choice can produce a source that produces predominately the P_4 molecular species rather than the desired P_2

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Growth of InP By Molecular Beam Epitaxy

Final Report

Earl L. Meeks and Fred L. Eisele

Period Covered 1 November 1980 - 28 February 1982

U.S. Army Research Office

Contract No. DAAG 29-80-K-0100

Georgia Institute of Technology
Engineering Experiment Station
Electromagnetics Laboratory
Physical Sciences Division
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1.0 INTRODUCTION

The research performed on this program was directed towards a basic materials study of indium phosphide growth by molecular beam epitaxy (MBE). Motivation for this investigation is based on theoretical and experimental studies which have shown that InP devices exhibit excellent performance at millimeter wavelengths (1,2). Indium phosphide is also being explored as a material for use in conjunction with ternary and quaternary alloy semiconductors for optoelectronic devices such as double heterostructure lasers.

Improvements in selected electrical characteristics of InP over GaAs have prompted research efforts to utilize InP rather than GaAs in millimeter wave transferred electron and IMPATT diodes. Conventional epitaxial growth systems such as liquid phase epitaxy (LPE) and vapor phase epitaxy (VPE) growth systems experience difficulty in reproducibly growing the very thin layers with abrupt n and p-type doping transitions which are required for such devices at millimeter wavelengths.

Molecular beam epitaxy is a semiconductor growth process which has rapidly matured in the last few years to the point where useful devices are being demonstrated, including GaAs FETs, IMPATTs, mixer diodes, double heterostructure lasers, and optical waveguides. Significant advantages which MBE provides over other epitaxial growth techniques are smoothness and uniformity of layers, extremely precise control of layer thicknesses and dopings, low epitaxial growth temperatures which minimize thermal diffusion effects, masking flexibility, versatility in selecting the chemical composition of the deposited epilayer, and capabilities for in situ surface analysis. These characteristics suggest the application of MBE to the growth of InP epitaxial layers for

millimeter wave devices with their extremely thin layers and abrupt n and p-type doping profiles.

2.0 EXPERIMENTAL DETAILS

2.1 Molecular Beam Epitaxy

Molecular beam epitaxy is a deposition technique which basically involves the condensation of beams of atoms or moleculares upon a heated substrate. Figure 1 schematically depicts a typical MBE system. The growth process is generally carried out under ultra high vacuum conditions at substrate temperatures which are generally lower than vapor phase or liquid phase techniques. The low substrate temperature minimizes undesirable thermal diffusion at interfaces in doping concentration or layer composition. Since typical growth rates are on the order of 3 A sec^{-1}, very abrupt changes can be injected in the growing eoilayer by mechanically shuttering the molecular beams projected from individually heated ovens containing elemental constituents and doping species. The in situ analyzers is in Figure 1 typically include reflection high energy electron diffraction (RHEED), low energy electron diffraction (LEED), Auger, and a quadrupole mass spectrometer. While most of the instruments are necessary in understanding surface characteristics, the wide diversity of equipment installed in successful MBE systems substantiates the point that a full complement of analyzers are not essential in growing layers for device applications.

2.2 Georgia Tech MBE System

The MBE system used for growth of the InP epitaxial layers was designed and fabricated at Georgia Tech explicitly for conducting research on III-V compound semiconductors. This system, one of five that have been designed and built at Georgia Tech, is an extremely versatile and reliable MBE system. This system has been used for the

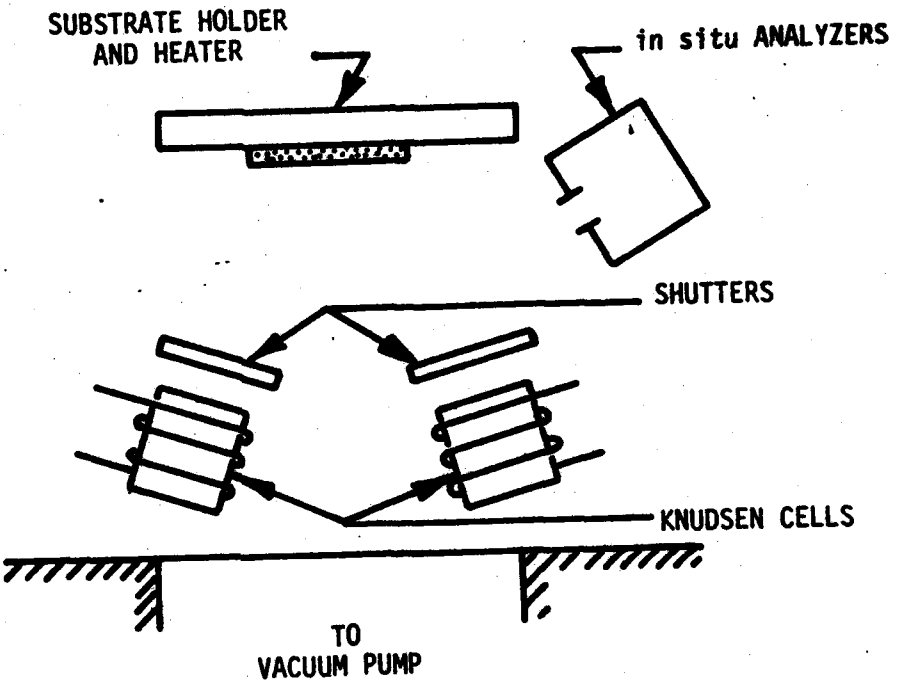


Figure 1. Molecular Beam Epitaxy System

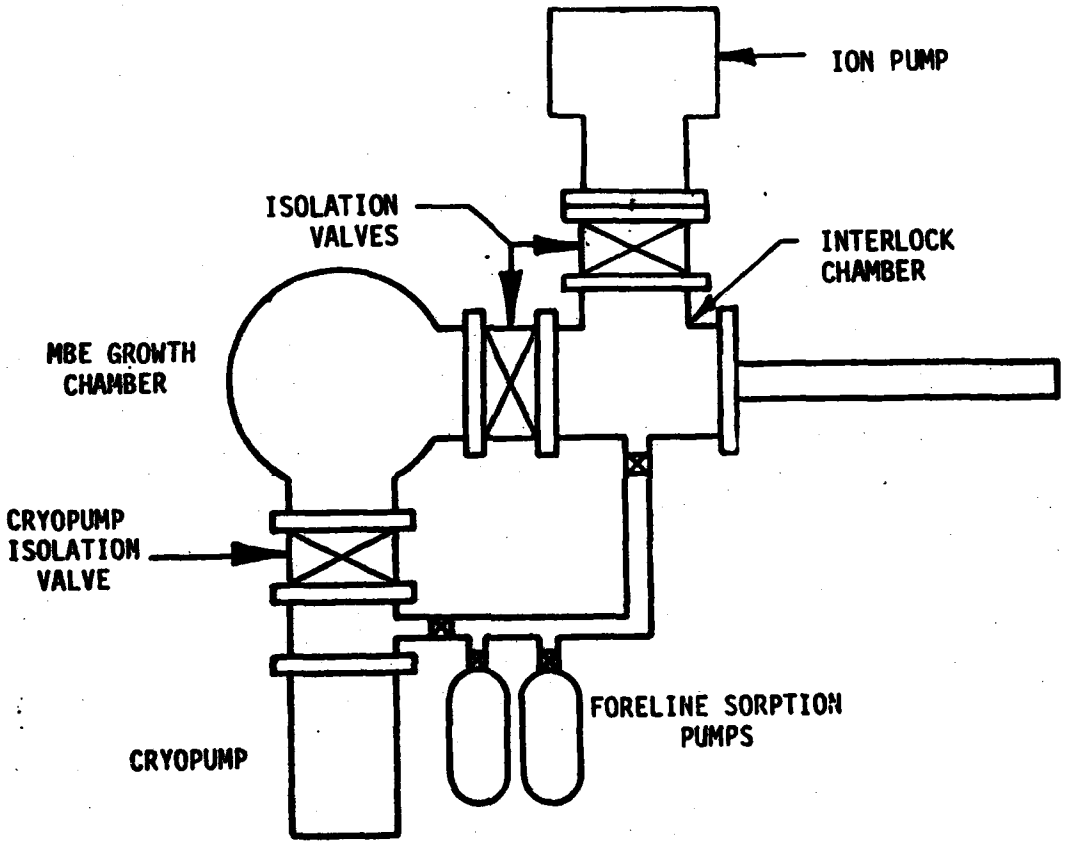


Figure 2. Details of Cryopump Connections for Evacuating the Growth and Interlock Chambers.

a fresh substrate. The pressure in the growth chamber does not change significantly when the main gate valve between the evacuated interlock and the growth chamber is opened.

Figure 3 is a cross-sectional drawing that shows the placement of the major components in the growth chamber. The six sources have rotational symmetry about the central axis of the chamber. The interior, unshaded area represents the cone-shaped volume behind the substrate that has direct exposure to all sources. The quadrupole mass spectrometer and ion gauge are mounted in the region of direct flux exposure. A LN_2 cryopanel surrounds the growth region to isolate it from the rest of the system and confine the effusing materials to as small a volume as possible.

A central viewport is available for viewing the epilayer during growth. Good MBE material is very smooth, and visual observations of the growing layer provide a valuable, noncontaminating diagnostic technique. The viewport also facilitates direct laser illumination of the substrate during in situ laser annealing studies.

The source ovens are made by cutting a thread groove in a Al_2O_3 tube deep enought to bury the Ta wire heater winding. A spectrographicaly pure graphite insert is made for each source and drilled so the remaining wall thickness is about 1.0 mm. The temperature control thermocouples are spot welded to Ta disks that are positioned at the bottom third of the source and held in position by another graphite insert drilled to fit the thermocouple insulating ceramic. Several layers of dimpled Ta foil wrapped around the ovens provided thermal isolation. These ovens are inexpensive, easy to build, and have been used for many years. They have been replaced recently by all Ta and pyrolitic boron nitride ovens in another of the Georgia Tech

MBE systems. Integration of the pyrolitic boron nitride ovens is planned for the InP system during the next year of the program.

2.3 Substrate Preparation

The InP substrates used were in almost all cases purchased already polished from CrystaComm Laboratories. The orientation was 2^{o} off the 100 toward the 110 and both Sn doped and Fe doped substrates were used as dictated by the application.

After scribing and breaking to size (1.5 cm x 2.0 cm), the substrates were solvent cleaned in boiling trichlorethylene rinsed in methanol and DI water, and blown dry with N_2. Further preparation included one minute etch each in 1:1:1 H_2SO_4: H_2O_2: H_2O and 1.0 % Br in methanol, followed by methanol and DI water rinse with N_2 blow dry. This cleaning procedure leaves the surface preferentially covered with an oxide which can be removed in the vacuum system by a pre-growth bake above $450^{o}C$ rather than covered with carbon which cannot be removed easily without ion bombardment. The cleaning procedure also removes about 20 m of material from the surface to eliminate damage that may remain from polishing.

The clean substrates were soldered to Mo carrier plates with six nines purity indium, and the carrier plates are mounted on the substrate heater. Each carrier plate has been drilled and tapped so the substrate heater thermocouple can screwed down to the carrier plate for good mechanical and thermal connection. A good mechanical connection between substrate carrier and thermocouple is mandatory to obtain reproducable temperature measurements.

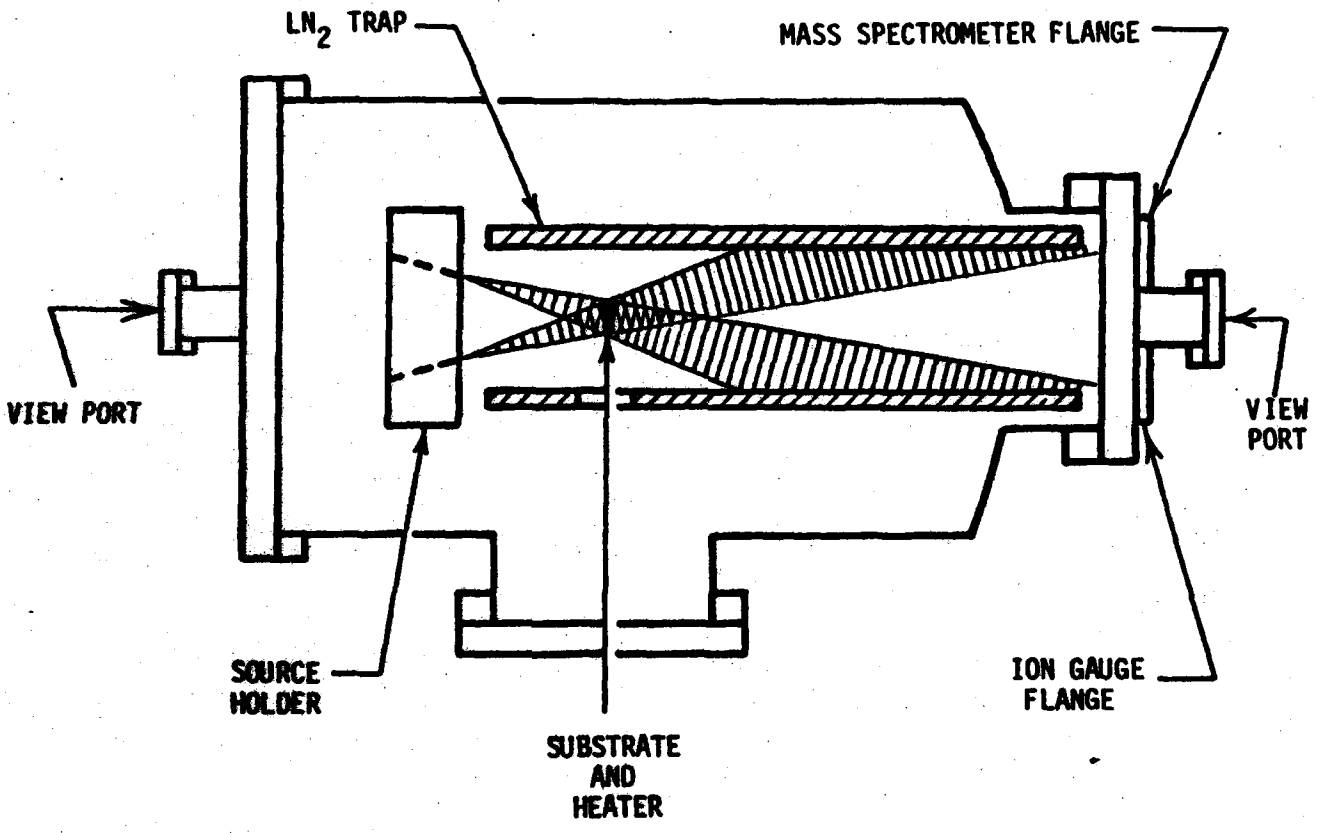


Figure 3. Major Components of the Growth Chamber of the Georgia Tech MBE System

2.4 Phosphorus Sources

The InP MBE work at Georgia Tech grew naturally out of our work on quaternary materials. The primary phosphorus source used for the quaternary layers was InP and the first InP MBE layers were grown using an InP phosphorus source. When growth was attempted with an elemental red phosphorus source, the layers were polycrystalline over a wide range of growth parameters. The significant difference between InP and red phosphorus is that InP yields primarily a P_2 molecular species while red phosphorus yields primarily P_4. Based on this observation an investigation of several different phosphorus sources was undertaken with the objective of finding a source that yielded a significant proportion of atomic phosphorus.

Calawa[3] has used arsine to grow very high mobility GaAs layers. The arsine, cracked under proper conditions in the vacuum system, produces a significant proportion of atomic arsenic. Similarly, cracking of phosphine in the Georgia Tech MBE system has been shown to produce a small proportion of atomic phosphorus. Drawings are shown in figure 4 of five phosphorus sources that have been investigated on this program. Three of these sources used phosphine introduced into the vacuum system through a controlled leak valve and cracked in various manners to provide the necessary phosphorus for growth. The first attempt used phosphine impinging directly on the heated substrate and produced polycrystalline layers. In the second source, Figure 4b, the phosphine was directed away from the substrate towards a very hot (1500°C) Ta ribbon filament that was exposed to the substrate. In the third source, Figure 4c, the phosphine was cracked in a plasma formed by an electric current passed through the gas as it was leaked into a small

heated chamber. The layers grown with the last two phosphine sources had specular surfaces but had poor mobilities. All of the phosphine sources had the same detrimental characteristic that the pressure in the system during growth went up to 10^{-5} Torr and remained at this level for 10-18 hrs after the phosphine leak valve was closed. This high pressure was not due to the H_2 produced in cracking PH_3 but the formation of white phosphorus which has a much higher vapor pressure than red phosphorus. The white phosphorus deposited on the cryopanels during growth and produced the 10^{-5} Torr pressure until the panels were warmed up after the run and the phosphorus slowly transferred to the cryopump walls. No acceptable procedure could be found to circumvent this problem and the phosphine sources were abandoned.

An attempt was also made to crack red phosphorus by passing an electric current through the phosphorus vapor to form a plasma. Red phosphorus was sealed in a double walled quartz tube with a small exit hole as shown in figure 4d. When the discharge occured, this source produced so much phosphorus that it immediately overpressured the 400 ls^{-1} ion pump on the test system. We were not able to continue work with this source due to time and financial limitations, so no growth runs were made for its evaluation.

The most successful phosphorus source found thus far has been InP in the small cell shown in figure 4e. The surfaces of the layers grown with this source are excellent, and the mobilities are the best that have been reported in the literature. However, these small cells are depleted after only 3-4 hrs of growth and the vacuum system must be opened to refill the source with InP. It has been our experience with MBE GaAs that the first run after the system has been opened and exposed

to air does not produce as good material as can be expected after several hours of operation. Therefore, due to the short life of the InP source, we have not achieved MBE InP material of the quality that should be possible with this system.

A larger InP source (Figure 4f) was not successful. The layers grown with this source were very similar to the layers grown with a conventional red phosphorus source. Quadrupole mass spectrometer measurements of the flux from the large InP source revealed it to be primarily a P_4 source, and thus it offered no advantage over the red phosphorus source.

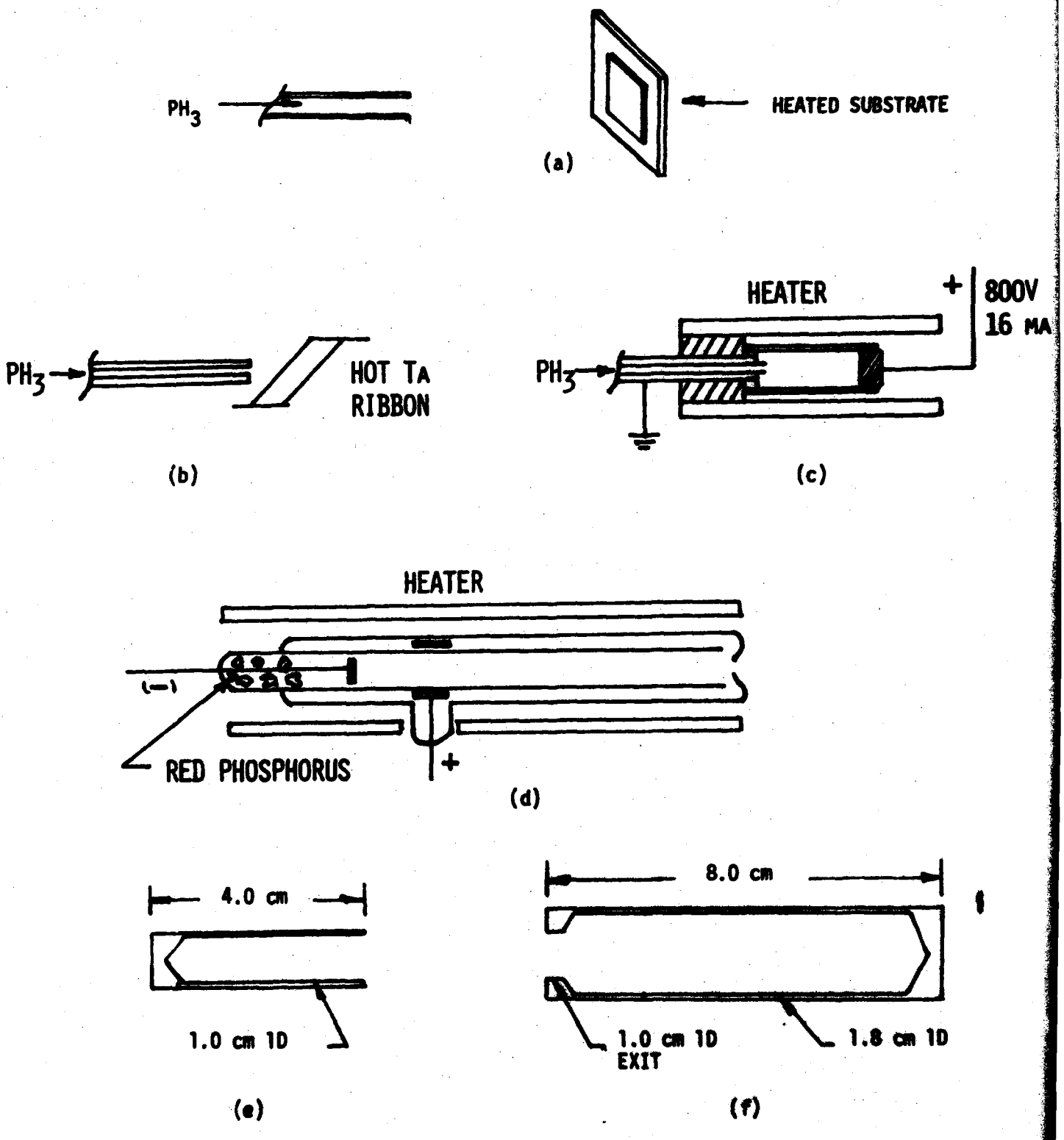


Figure 4. Phosphorus Sources.

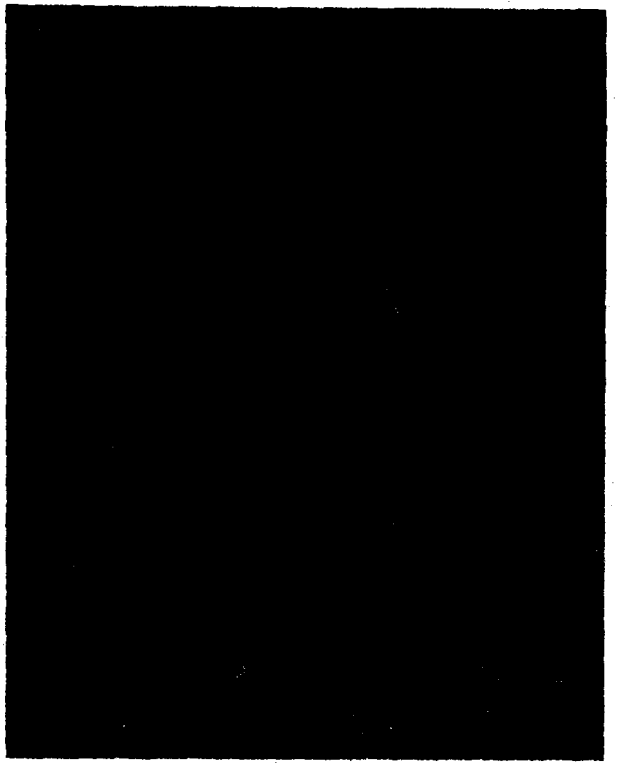
3.0 RESULTS

3.1 Optical Surface Evaluation

Many attempts were made to grow InP MBE layers with a conventional red phosphorus source; the typically poor surface quality is shown in figure 5A. The surface shown in figure 5B was grown under identical conditions with substrate temperature of 480C but with the small InP source. The surface 5B looks mirror smooth with the unaided eye but a slight oriented structure can be seen at 500X. At a substrate temperature of 530^{0} this structure disappears and the surface is featureless at 500X. Figure 5C shows the surface of a layer for which growth was initiated with the InP source for 30 min, and then the red phosphorus source flux was added for 30 min more growth. The growth was terminated with 30 min growth using the red phosphorus source only. The surface of the growing layer can be continuously observed visually during growth in the Georgia Tech MBE system and was clear as long as the InP flux was present. Soon after the last 30 min of growth was initiated with only the red phosphorus flux the surface clouded over with the results as shown in Figure 5C. The surface in figure 5C is better, however, than that shown in 5A, so some advantage was achieved in initiating growth with the InP source.

3.2 Hall Measurements

Typical temperature dependence of the Hall mobility is shown in figure 6 for three layers. Ionized impurity scattering is responsible for the decrease in mobility below 100K. These three layers were grown using InP for a phosphorus source. Other measurements are shown in table 1 which includes layers grown with InP and plasma cracked phosphine sources. All layers grown using cracked phosphine had very



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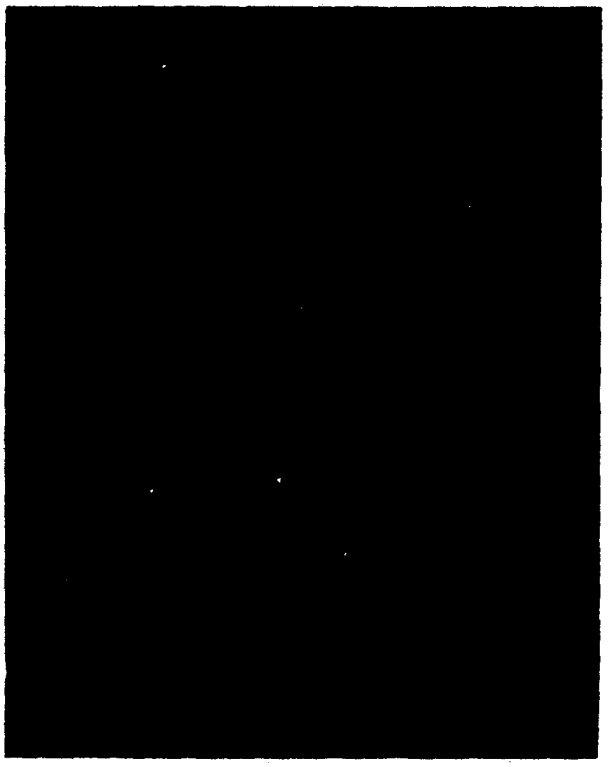
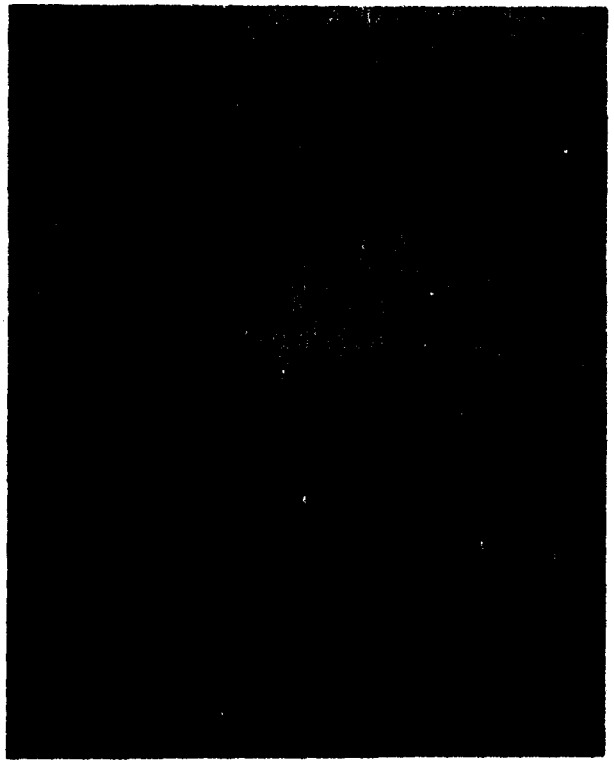


B



C

A - 21 MIN P_4 GROWTH
B - 60 MIN. P_2 GROWTH
C - 30 MIN P_2, 30 MIN. P_2+P_4, → 30 MIN P_4

500x

Figure 5. InP Epilayer Surfaces.

poor mobility. It was very difficult to make meaningful mobility measurements on the layers grown using cracked phosphine because our usual ohmic contact procedures did not produce good, uniform ohmic contacts. Low temperature mobility measurements are particularly difficult with poor quality contacts. All the material for the phosphine grown layers was consumed in different ohmic contact procedure trials before reliable low temperature measurements were obtained.

3.3 Manganese Doping

Three runs were made introducing Mn during growth for a p-type dopant. All of the unintentionally doped material grown in the system was n-type and ohmic contacts were easily made to this material. In contrast, all metal contacts evaluated (Au-Ge, Au-Mn In-Zn & Ag-In-Mn) on the Mn doped material were highly rectifing. The bias on these rectifying contacts indicated the Mn doped material to be p-type, but all the material was consumed before proper ohmic contacts could be made and no Hall data were obtained. No additional effort was possible on this task during this period due to financial constraints.

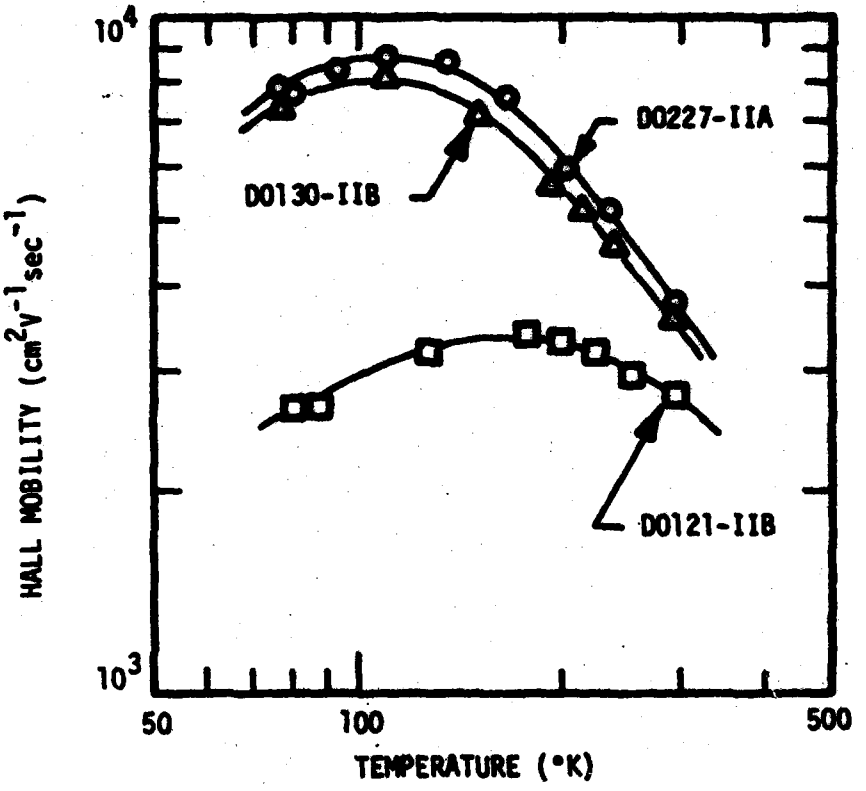


Figure 6. Hall Mobility vs. Temperature for Unintentionally-Doped MBE InP Layers.

4.0 CONCLUSIONS

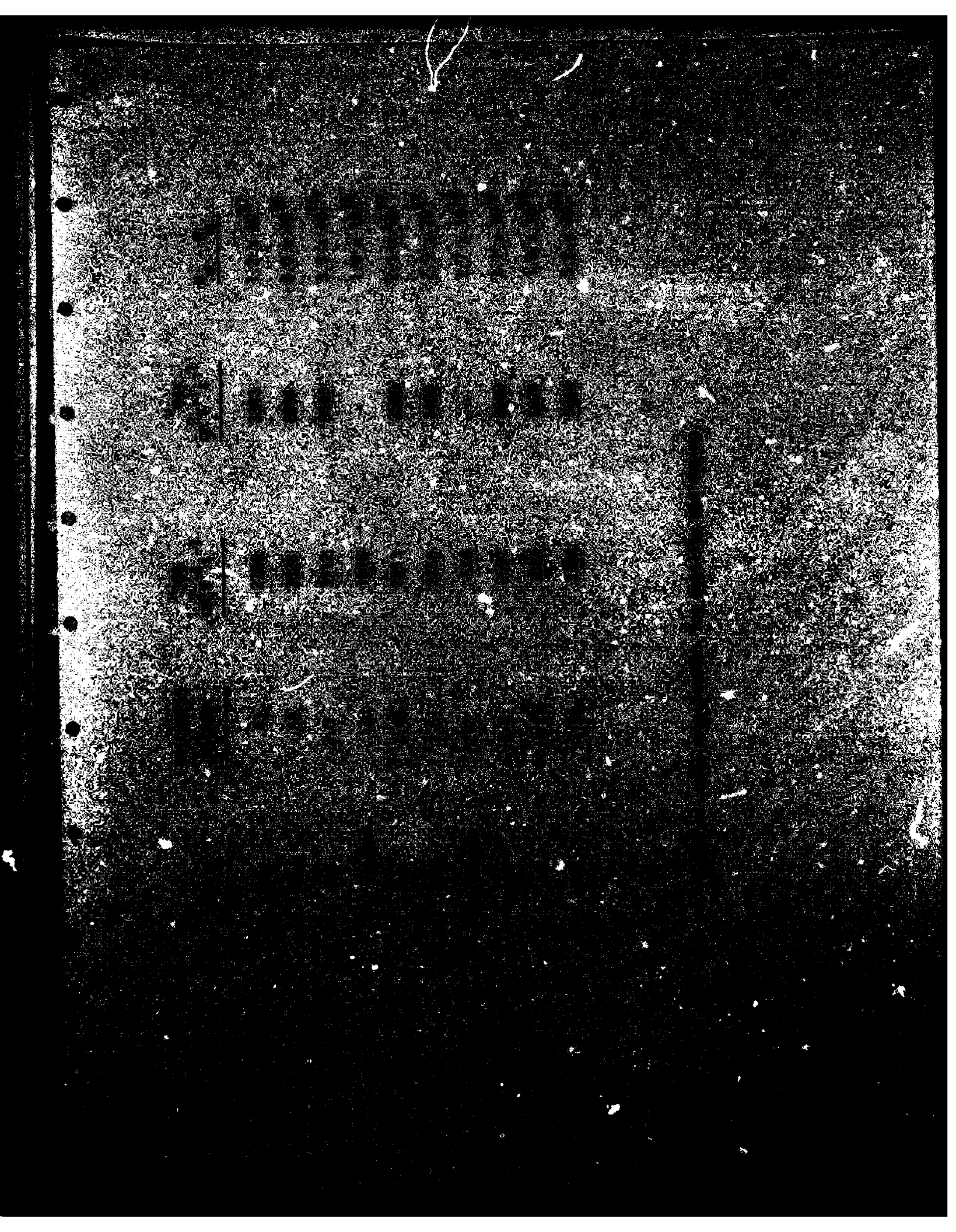
Indium Phosphide MBE layers have been grown using a number of different phosphorus sources. Sources that produce a significant flux of P_2 or atomic phosphorus yield much higher quality epitaxial films than sources which are predominantly P_4. The best materials grown to date had room temperature mobilities greater than 3700 $cm^2V^{-1}s^{-1}$ and were grown using a small InP phosphorus source. The geometry of the InP phosphorus source is important. An incorrect choice can produce a source that produces premoninately the P_4 molecular species rather than the desired P_2.

It may be possible to use phosphine as a phosphorus source if one can discern a way to circumvent the associated problem of maintaining a good vacuum in the growth chamber.

First indications are that Mn may be an acceptable p-type dopant for MBE InP. Much more work would be necessary for a complete evaluation.

The effort described in this report will be continued on a follow-on program whcih will begin in August 1982. Emphasis on this program will be as follows:

- o develop a P_2 source by cracking red phosphorus
- o integrate PBN ovens to reduce the system unintentional background doping level
- o continue investigation of dopants.



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