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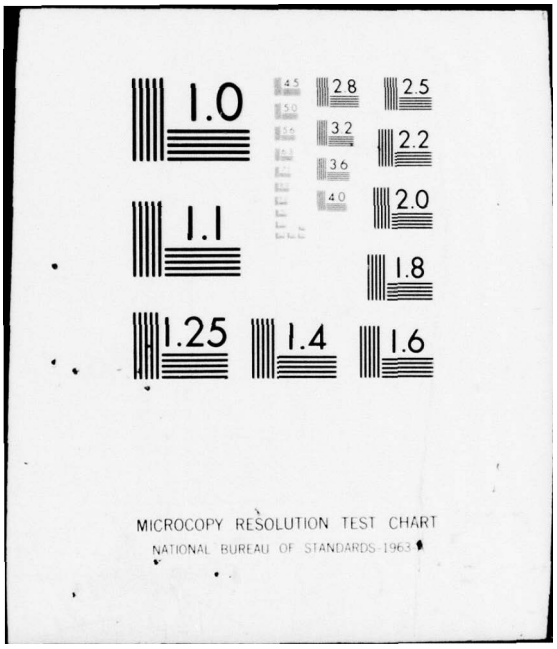
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INDIUM PHOSPHIDE FOR MICROWAVE GUNN DEVICES

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Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, California 90265

July 1977

Contract No. F44620-76-C-0133
Interim Report
For Period June 1976 through June 1977

Prepared for
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling Air Force Base
Washington, D.C. 20332

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(19) REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) AFOSR TR-77-0944	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) INDIUM PHOSPHIDE FOR MICROWAVE GUNN DEVICES.	5. TYPE OF REPORT & PERIOD COVERED: INTERIM
(10)	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Fraas, Lewis / Zanio, Kenneth / Fraas / Zanio	8. CONTRACT OR GRANT NUMBER(s): new (15) F44620-76-C-0133
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, California 90265	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61102F 2306-B1 (16)
11. CONTROLLING OFFICE NAME AND ADDRESS: AFOSR/NE, Bldg 410, Bolling AFB, DC 20332 (12) 39 p. (11)	12. REPORT DATE: June 1977 (17)
	13. NUMBER OF PAGES: 37
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLAS
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

(9) Interim rept. Jun 76 – Jun 77,

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Indium phoshide,
transferred electrom device
planar reactive deposition

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

One-micron-thick films of InP were epitaxially deposited onto single-crystal InP substrates at about 400 C by the planar reactive deposition technique. Scanning electron microscope measurements show that smooth surfaces are obtained on (100) substrates, and shingled surfaces are obtained on (111) substrates. Mass spectrographic analysis indicates that the purity of these films is about 10 parts per million atomic. Electrical evaluation of these films deposited on semi-insulating substrates shows that at room temperature the

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20. films are n-type with electron concentrations as low as 10^{16} cm^{-3} and mobilities as high as 1350 cm^2/V sec.

FOREWORD

This report was prepared by Dr. Lewis Fraas and Dr. Kenneth Zanio, the principal investigators on the program, of the Hughes Research Laboratories, a division of Hughes Aircraft Company, for the Air Force Office of Scientific Research under contract number F44620-76-C-0133. The contracting personnel at AFOSR are Capt. Wayne Steinbach and Dr. Larry Kravits.

The program is being undertaken in the Exploratory Studies Department and the Chemical Physics Department under the supervision of Dr. D. Close, Dr. G.S. Picus, Dr. D. Pinnow, and Mr. L. DeVaux. The project head is Dr. Fraas. Important contributions were made by Messrs. F. Krajenbrink, H. Montano, and P. Hoberg.

ABSTRACT

One-micron-thick films of InP were epitaxially deposited onto single-crystal InP substrates at about 400°C by the planar reactive deposition technique.

Scanning electron microscope measurements show that smooth surfaces are obtained on (100) substrates, and shingled surfaces are obtained on ($\bar{1}\bar{1}\bar{1}$) substrates. Mass spectrographic analysis indicates that the purity of these films is about 10 parts per million atomic. Electrical evaluation of these films deposited on semi-insulating substrates shows that at room temperature the films are n-type with electron concentrations as low as 10^{16} cm^{-3} and mobilities as high as 1350 cm^2/V sec.

10 to the 16th power/cu cm

1350 sq. cm/V sec.

TABLE OF CONTENTS

SECTION 1

INTRODUCTION

A. RESEARCH OBJECTIVES

The following interim report describes the work undertaken at Hughes Research Laboratories (HRL) to investigate InP as a material for transferred electron devices (TEDs). The specific research objectives of this program are to:

- Prepare InP substrates for epitaxial deposition of InP
- Optimize planar reactive deposition (PRD) growth parameters for InP epitaxy on InP
- Grow doped n-type layers
- Evaluate InP epitaxy by structural, electrical, and optical measurements
- Provide InP films to Air Force Office of Scientific Research (AFOSR) for evaluation.

B. SIGNIFICANT ACCOMPLISHMENTS

This program has demonstrated that the planar reactive deposition (PRD) technique is a viable deposition technique for fabricating semiconductor-quality epitaxial InP thin films. We found that mirror-smooth epitaxial InP films 2-μm thick can be reproducibly grown on (100) InP substrates at temperatures as low as 350°C and that these films possess electron mobilities as high as 1350 cm^2/V sec and electron concentrations as low as 9×10^{16}/cc. An InP film having comparable electrical properties has been delivered to AFOSR for evaluation.

This report describes the construction and operation of the PRD machine. Thin-film morphology studies, impurity analyses, and electrical evaluation are also described.

SECTION 2

PLANAR REACTIVE DEPOSITION SYSTEM

A. DESIGN AND CONSTRUCTION

Figure 1 shows the PRD machine constructed by HRL. This machine is dedicated to InP thin-film studies. The PRD process (described in Ref. 1) is performed in a metal vacuum chamber evacuated to 10^{-8} Torr. Metals or alloys of metals are melted in a planar Knudsen cell enclosed by a cold shroud (Figure 2); this reduces the concentration of condensable gases by at least another order of magnitude. Hydrogen provides a reducing atmosphere and reduces oxygen incorporation in the InP growing films. A nonmetal is introduced into the cell as a gas (such as P introduced as PH_3); the gas decomposes in the cell. During InP deposition, In, P_2, and H_2 molecular beams stream onto a cooler substrate to form InP.

Figure 3 shows the top view of the chamber design for the PRD system of Figure 1. Features of our new PRD system include (1) provision for incorporating reflection electron diffraction (RED) and ion beam etching systems, (2) incorporation of a Knudsen cell, (3) more effective source chamber design, and (4) two source-evaporation chambers instead of one. This two-source design will allow forming $n^+/n/n^+$ structures without breaking vacuum.

Control over the growth process is important where thin layers, abruptness, or specific doping profiles are required. The PRD technique allows using a variety of in situ monitoring techniques not available in CVD processing (e.g., residual gas analysis, thickness monitoring, and RED).

B. IMPURITY GAS STUDIES

The PRD machine built for InP work (shown in Figure 1) is equipped with a residual gas analyzer (CVC Quad 1210, 0 to 100 amu). This allows identifying impurity gases before, during, and after InP film deposition. This is illustrated by Figure 4, which shows

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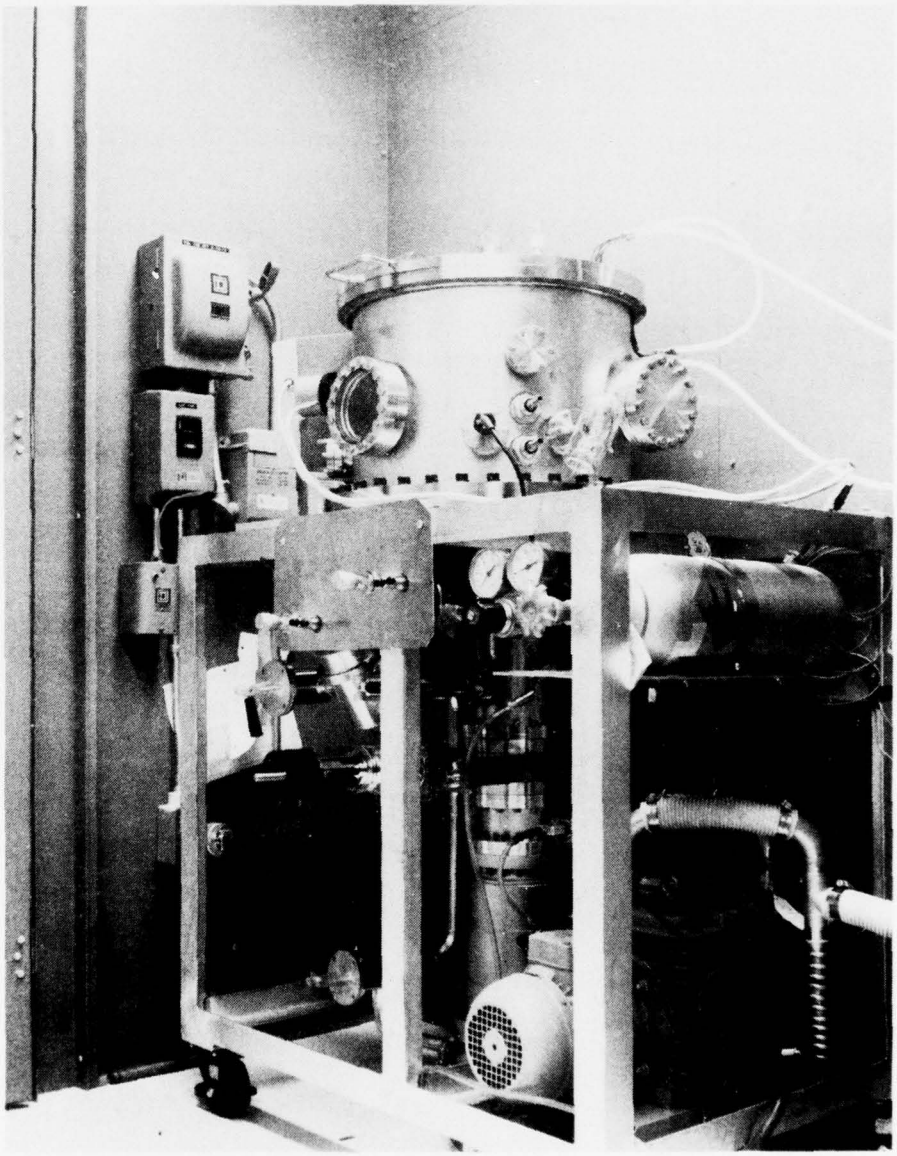

Figure 1. New PRD system for the deposition of InP thin films.

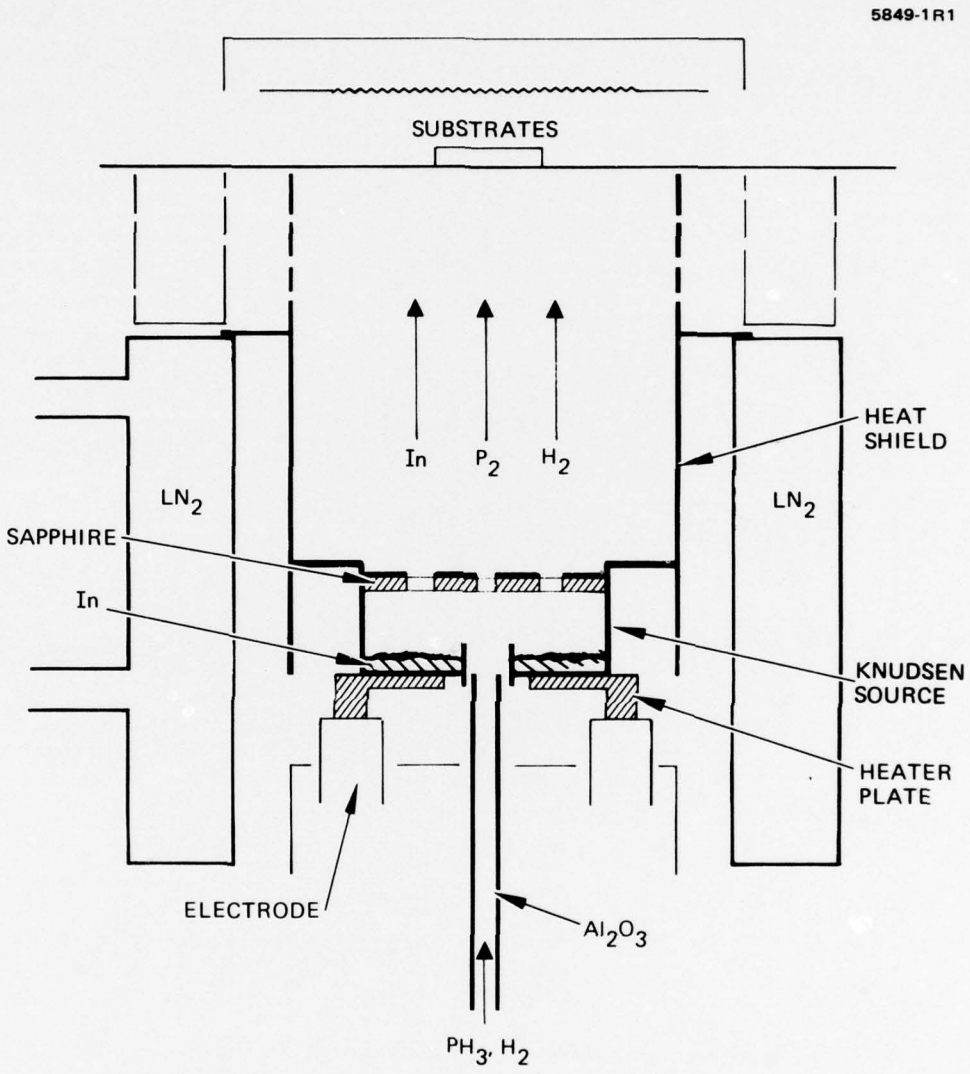

Figure 2. New shroud design in deposition chamber of PRD system.

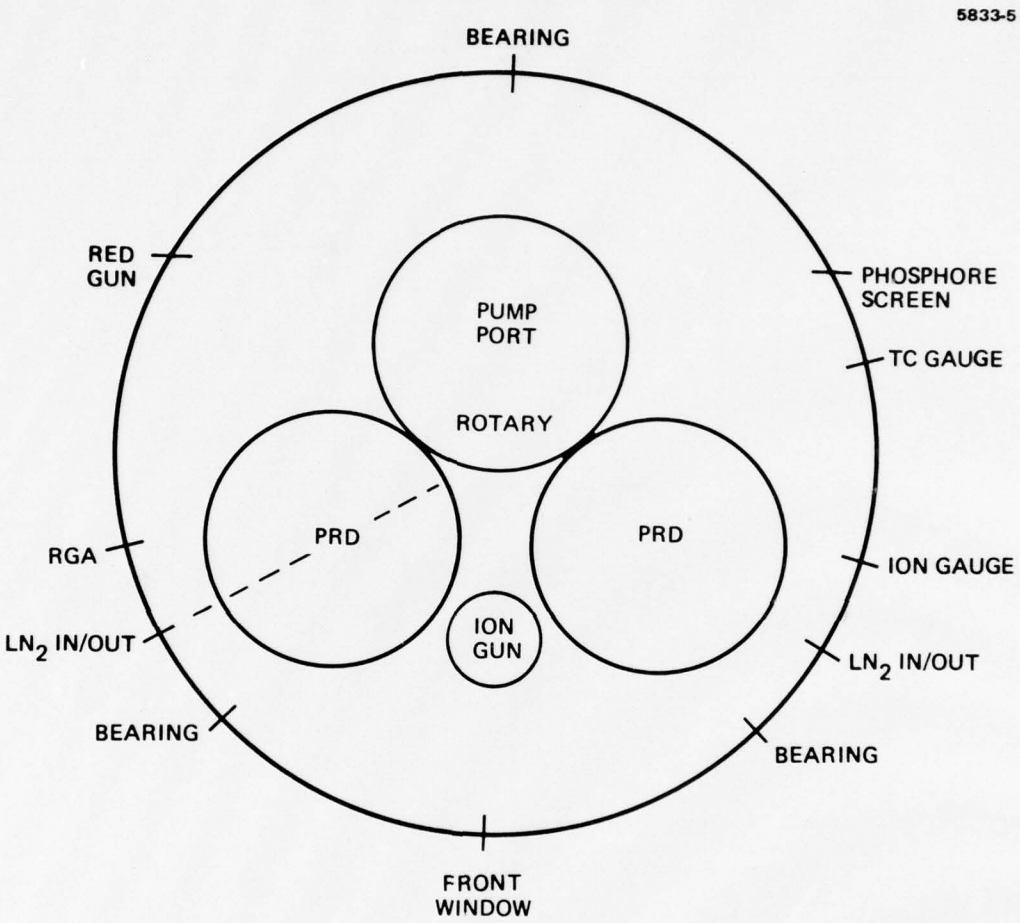

Figure 3. Vacuum chamber top view for PRD system. The dashed line in this drawing represents the cross section shown in Figure 2.

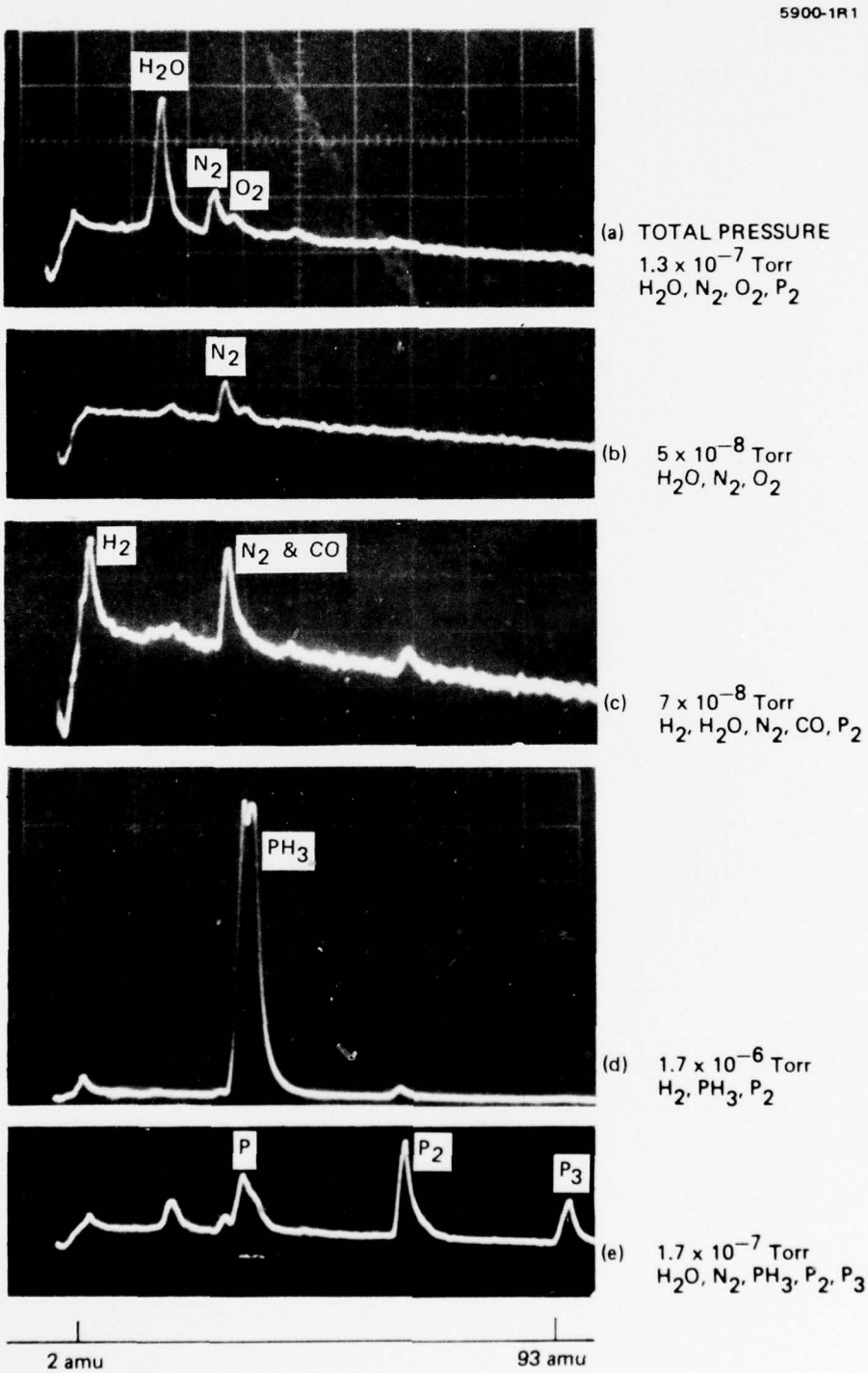

Figure 4. Residual gas spectra for vacuum chamber after (a) sample loading, (b) filling LN_2 shroud assembly, (c) source outgassing, (d) $H_2 + PH_3$ gas shutoff at end of film deposition, and (e) LN_2 shroud emptied at end of deposition.

spectra (a) after sample loading, (b) after adding liquid nitrogen to the shroud, (c) after source outgassing, (d) immediately after film deposition, and (e) just prior to sample unloading.

There are three points worth noting in these spectra. First, adding LN_2 does lower the condensable gas pressure (H_2O) by an order of magnitude. Note the decrease in H_2O peak intensity from (a) to (b). Second, the source can be outgassed to the degree that it contributes negligible contaminants to the growing film. Note that the H_2 peak is the only new peak present in (c). This new peak accounts for the rise in pressure between (b) and (c). Third, the total pressure in the system can be reduced to the 10^{-9} Torr range by simply repairing the 10^{-8} Torr air leak. This has now been done, but this air leak problem was given low priority during the morphology studies.

These experimental observations support the earlier design assumptions made when the PRD process was proposed. The conclusion is that the PRD technique, like the molecular beam epitaxy technique, is capable of producing a clean environment for the growth of high-purity semiconductor films.

C. PRINCIPAL ADVANTAGES OF PRD

The PRD technique, invented and developed by HRL, is a hybrid between the ultrahigh vacuum (UHV) molecular beam technique and the chemical vapor deposition (CVD) technique.[1,2] Thus, PRD is capable of economically depositing thin epitaxial semiconductor films at low temperatures with excellent thickness and doping control. Since 2-μm-thick epitaxial (100) films are n-type and mirror-smooth, they are potentially useful for TEDs. Five of the principal advantages for fabricating TED devices with PRD are discussed below:

- The low substrate deposition temperature facilities abrupt n^+-to-n interfaces. The potential result is low $n^+/n/n^+$ series resistance and high power efficiencies.

- Since it is a vacuum technique, thickness can be monitored in situ with a crystal oscillator. The result is angstrom-scale thickness control.

- Excellent doping control can be achieved because doping is done by evaporating an In:Sn alloy and because the indium and tin vapor pressure curves run parallel as source temperature varies. Consequently, a source temperature increase of $60^{\circ}C$ results in an order of magnitude increase in the InP film-deposition rate without the dopant concentration changing. Excellent doping control, combined with good thickness control, will potentially lead to devices with excellent oscillator frequency reproducibility.

- The PRD technique is easily scalable. Thus, 50 $in.^2$ of 5-μm-thick InP devices can be easily produced in one day in a standard 18-in.-diameter vacuum chamber.

- The PRD technique, like the CVD technique, operates with reducing hydrogen gas. This may potentially lead to higher purity films than those obtained with MBE. Thus, since the CVD technique has been used to produce pure epitaxial layers for TEDs, the PRD technique can produce thinner layers with more abrupt interfaces.

SECTION 3

MORPHOLOGY STUDIES OF InP FILM

The structural features of InP thin films deposited by PRD have been studied using the scanning electron microscope (SEM), and the PRD process variables and sample-preparation procedures have been optimized. The process conditions currently used are outlined in this section. Nine of the last ten samples processed have shown good epitaxy.

A. OPTIMUM DEPOSITION CONDITIONS

1. Substrate Chemical Preparation

Saw-cut 1.5-in.-diameter InP wafers obtained from Cambridge/IMANCO and Varian Associates are diced into 3/8 x 3/8 in. squares and then mounted with indium solder on 1/4 in. high, 5/8 in. diameter cylindrical molybdenum blocks. Each InP sample is mounted so that the (100) or $(\bar{1}\bar{1}\bar{1})$ face is exposed for chemical polishing. The samples are polished by hand with a 5% bromine in methanol solution. The solution is applied to a lens paper pad on a glass plate. This yields an optically smooth surface after approximately 3 to 5 min. The samples are then rinsed and stored in electronic-grade methanol. The samples, just before being loaded, are etched for 10 min in a 0.5% Br:methanol solution, then rinsed in methanol and 10 MΩ deionized water. The samples are then spun dry and set into the sample plate in the PRD chamber.

2. Preparation of Thermally Etched, Phosphorus-Stabilized Substrate Surfaces

As discussed in our original PRD proposal, InP surfaces cannot be thermally cleaned in UHV without depleting the surface of phosphorus. We proposed re-supplying the depleted phosphorus by thermally etching the InP surface in the presence of an $H_2 + P_2$ beam. This procedure

was successful; corroborating data was recently published by Farrow.[3] The result is that InP surfaces can be thermally cleaned in a reproducible fashion. Sputter cleaning and annealing are not required.

3. InP Epitaxial Film-Deposition Conditions

A standard deposition begins with loading the substrates and positioning the substrate plate so that the source beam does not impinge on the substrates. The source is then turned on and thermally outgassed at approximately 850°C. After outgassing, the H_2 and PH_3 gas mixture is introduced. The source is then turned down and the substrates are rotated into position above the source in the presence of excess P_2. The substrate temperature is raised to ≈ 375°C, and the substrates are thermally cleaned. The substrate temperature is lowered to ≈ 325°C, and, simultaneously, the source temperature is raised along with the $H_2 + PH_3$ pressure. The source temperature and $H_2 + PH_3$ gas pressure are set such that stoichiometric InP films are deposited at a rate of 1.5 μm/hr. The source temperature is lowered after the first deposition. At this point, an additional set of samples can be rotated into position for thermal cleaning and InP film deposition.

B. RESULTING InP THIN-FILM MORPHOLOGY

The varieties of InP film morphologies obtained to date are shown in Figures 5 and 6. Figure 5 shows InP films on glass, (100) GaAs, and (100) InP. The difference between a polycrystalline film on glass and the epitaxial films on GaAs and InP is clearly evident. In Figure 6, the epitaxy of InP on a $(\bar{1}\bar{1}\bar{1})$ face is contrasted with the epitaxy of InP on a (100) face. The (100) epitaxial films are quite smooth in the SEM photographs and mirror smooth to the eye. A good epitaxial film can be so smooth that it is visually difficult to determine if a film is really present. The microprobe data in Figure 7 corresponds to the photographs in Figure 5. This data shows that an InP film has been deposited on the GaAs substrate. Figure 6 shows the presence of indium microdots on the surface of the $(\bar{1}\bar{1}\bar{1})$ sample. These dots form if the $H_2 + PH_3$ pressure is too low during the thermal-etch or film-growth processes.

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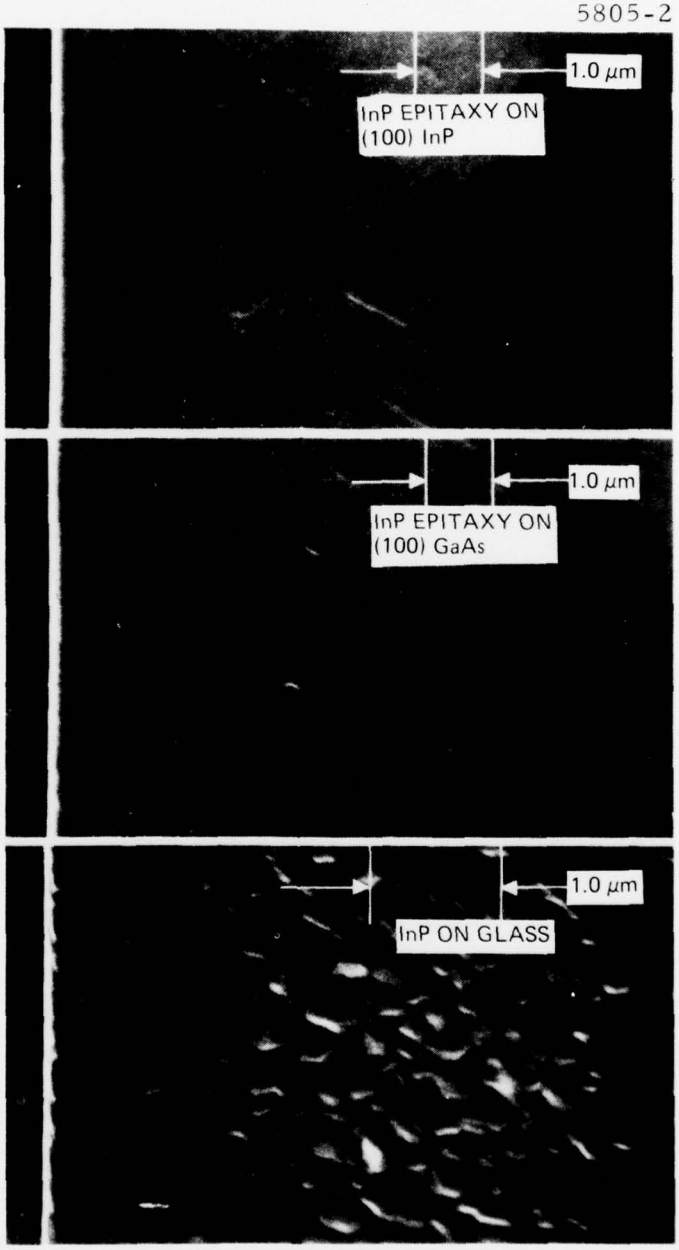

Figure 5.
SEM photograph of (a) epitaxial deposition of InP on a (100) InP substrate, (b) epitaxial deposition of InP on a (100) GaAs substrate, (c) deposition of InP on glass.
on glass.

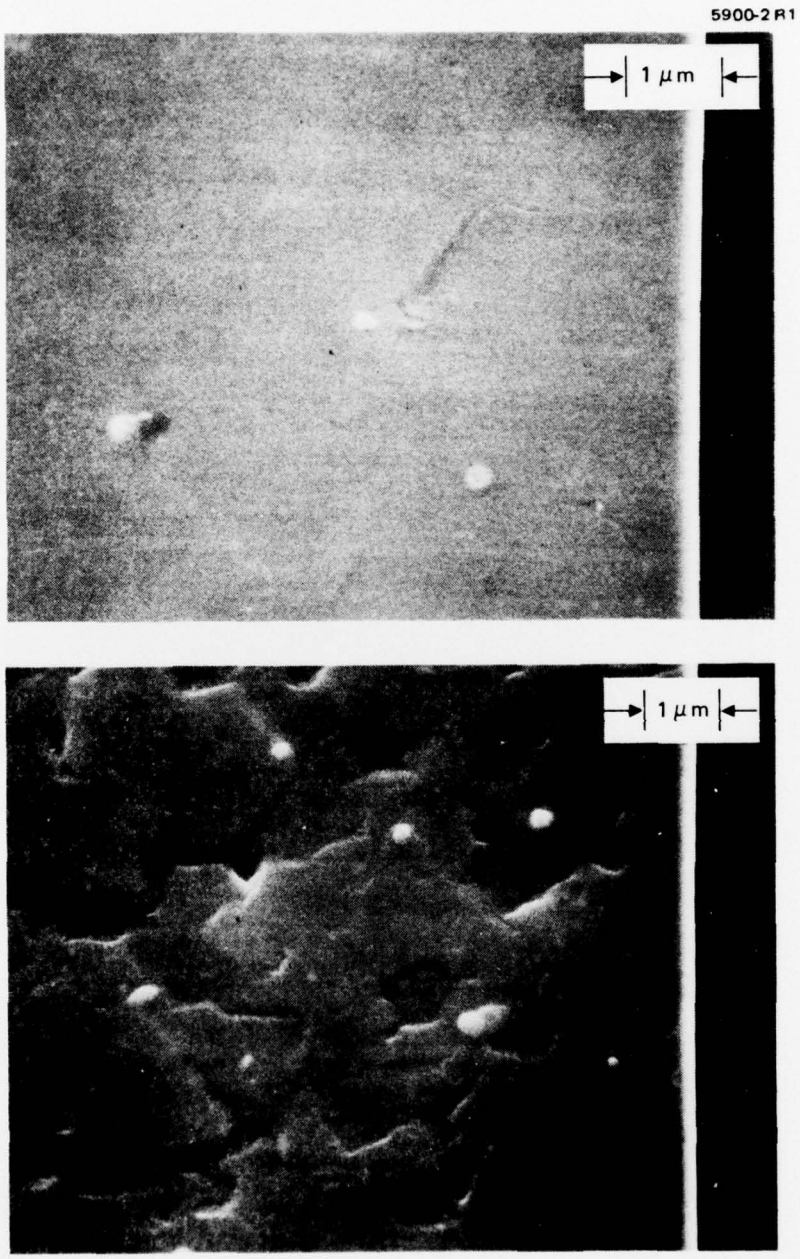

Figure 6. SEM photographs of (top) smooth InP epitaxy on (100) InP and (bottom) shingled InP epitaxy on $(\bar{1}\bar{1}\bar{1})$ InP.

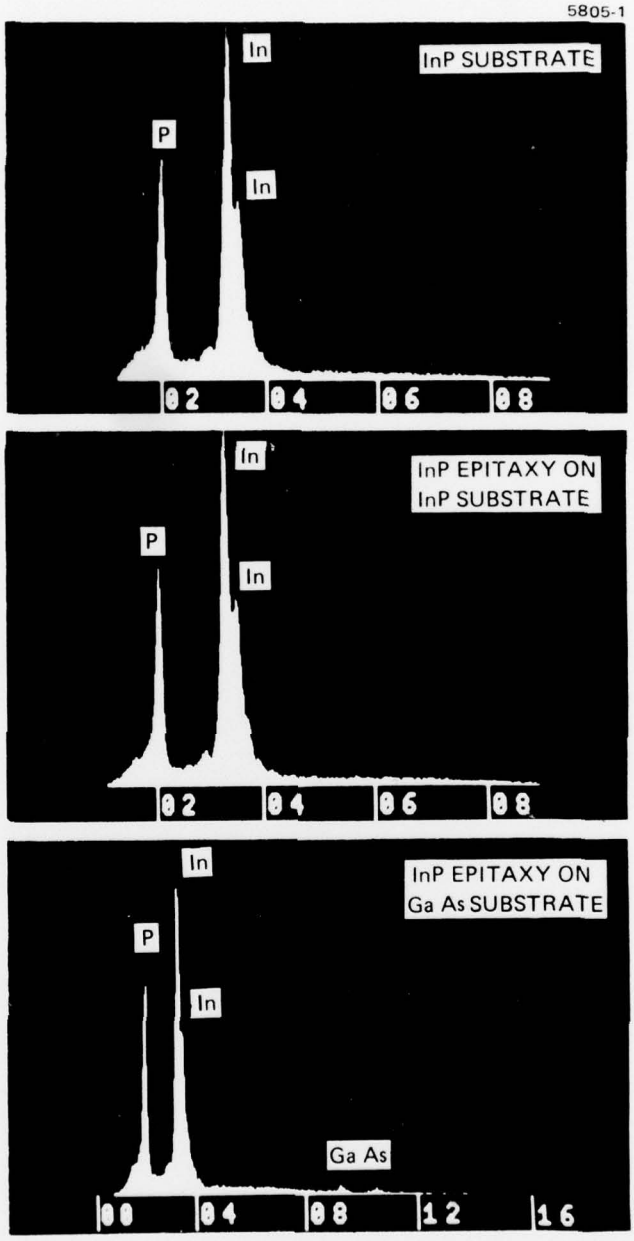

Figure 7.
Microprobe measurements of (a) an InP substrate, (b) the epitxial deposition of InP the same InP substrate, (c) the epitaxial deposition of InP on a GaAs substrate.

SECTION 4

ELECTRICAL EVALUATION OF InP FILMS

The best room temperature mobility was obtained for samples in run 24/3. A room temperature mobility of 1350 cm^2/V sec was obtained. Films were n-type with a free carrier concentration of 6×10^{17}/cc.

A. HALL MEASUREMENTS

Figure 8 shows Hall mobility and carrier concentration as a function of temperature for a sample from run 24/3. The notable feature is that no carrier freeze out occurred down to 15°K, suggesting a shallow impurity like Sn, S, Se, or Te.

B. MASS SPECTROGRAPHIC ANALYSIS OF FILM IMPURITY CONTENT

Table 1 summarizes the preliminary mass spectrographic analysis of a 5-μm-thick InP film deposited on a single-crystal silicon wafer. The cleanliness of the PRD method is about 10 ppma.* The main impurity appears to be sulfur at 6 ppma. Since 6 ppma would correspond to 2.5×10^{17}/cc free carriers, this data is roughly consistent with the electrical data measured for run 24/3.

C. PROBABLE IMPURITY SOURCES

There are four main sources of impurities in PRD-grown InP films: (1) the source and heat-shield assemblies, (2) the vacuum chamber residual gases, (3) the indium source, and (4) the PH_3/H_2 gas. However, during this period InP was also deposited onto CdS for

*An earlier mass spectrographic analysis showed 20 ppma Fe, which we attribute to the iron screws initially used in the system. Since then the iron screws have been replaced with Mo. Mass spectrographic analysis by two vendors showed less than 1 ppma of Mo despite the fact that Mo is extensively used for source heat shielding.

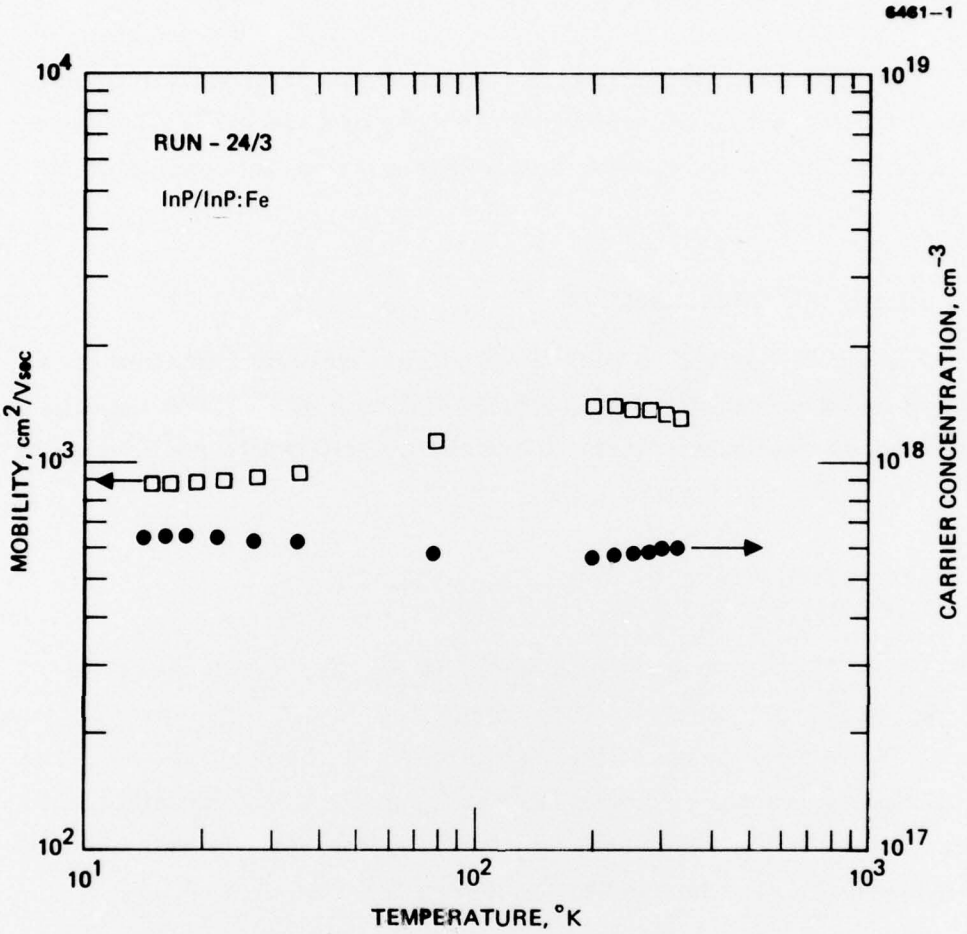

Figure 8. Mobility and carrier concentration for InP measured on semi-insulating InP:Fe substrate.

Table 1. Mass Spectrographic Analysis of a 5-μm-Thick Film of InP deposited on Si by PRD

Element	Concentration, ppma	
	InP Film	Si Substrate
B	0.05	0.5
C[R]	3.0	5.1
O[R]	3.4	6.5
F	1.4	2.1
Mg	1.7	1.0
S	6.4	1.0
CL	2.4	2.1
Ti	0.3	0.1
Cr[R]	0.2	0.4
Cu	1.0	0.4
Mn	1.5	2.0
Zn	0.1	0.05
Ba	1.5	ND
Fe	ND	ND
Mo	ND	ND
Ga[R]		
As[R]		
Be	IL	IL
N	IL	IL
Na	IL	IL
Sc	IL	IL
Co	IL	IL
Nb	IL	IL

IL – Interfering lines
R – Residual

solar-cell applications. Therefore, CdS represent an additional source of impurities. Since sulfur seems to be the residual impurity, it probably is introduced either with the PH_3/H_2 gas as an impurity or via CdS thermal dissociation.

SECTION 5

SUMMARY

Indium phosphide films of good quality were epitaxially deposited onto InP substrates by PRD. Although the residual electron concentration and mobilities were acceptable, higher purity films are necessary before TED devices will be feasible.

SECTION 6

FUTURE WORK

Future work will require careful coordination of experiments utilizing substrates other than InP. In continuing programs we intend to emphasize studies that may lead to improved purity. Specific studies directed towards this goal are to

- Install a pyrolytic boron nitride crucible and upgrade our heat-shield design in the planar reactive deposition apparatus
- Intentionally introduce CO in the gas stream and monitor the film quality as an approach of isolating the source of impurities
- Undertake mass spectrographic analysis of the InP films
- Lightly dope the In source with Sn to achieve n-type films with electron concentrations of the order of 10^{16} cm^{-3} and less.

SECTION 7

PROPERTIES OF DELIVERED InP FILM

In run 24/3, 2-μm-thick InP films were deposited on 1 cm^2 Fe doped (100) InP substrates. The substrates were mounted on molybdenum blocks. Electrical data for one of these samples is given in Section 4, Figure 8. A representative sample from this lot was delivered to AFOSR. Figure 9, a photograph of that sample, shows the surface of the deposited film to be mirror smooth.

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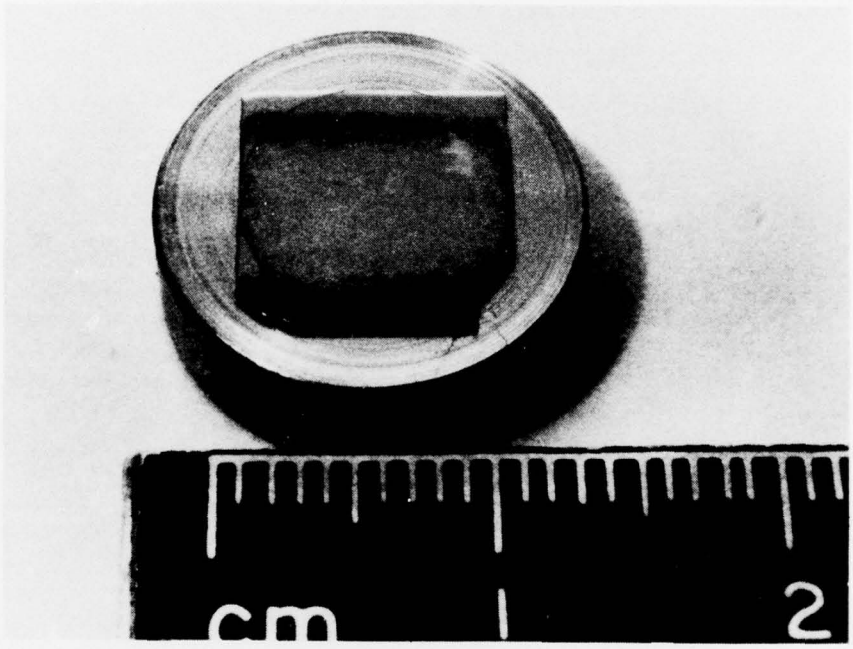

Figure 9. Epitaxial deposition of InP (circular) on InP substrate (square).

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3. R.F.C. Farrow, J. Phys. D 8, L87 (1975).

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2. "Epitaxial Layers of Ge on Ge and GaAs Substrates by Planar Reactive Depositions," K. Zanio, L. Fraas, and F.Krajenbrink. Submitted to J. Vacuum Technology.