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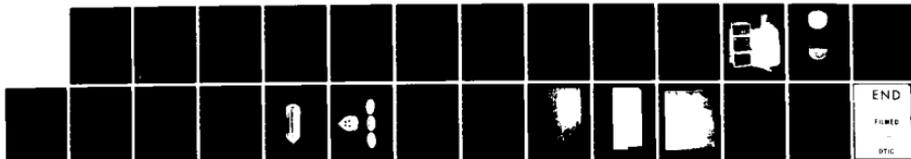
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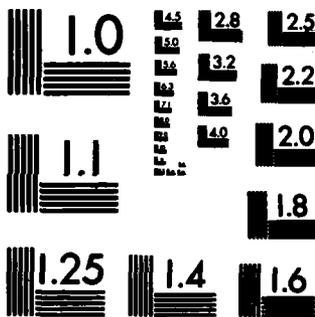
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Investigation of Liquid Encapsulation
Chochralski Growth of InP

Final Report for Period: July 1981 to June 1984

G.A. Antypas

August 1984

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Contract #DAAG29-81-C-0013

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Process have been developed (a) to synthesize polycrystalline InP by the injection of Phosphorus to B_{2O_3} encapsulated Indium and (b) to grow reproducible (100) oriented 7.5 cm diameter InP single crystals. These processes can be easily scaled up to yield crystals weighing up to 4 kilograms.		

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I. Introduction

A. Background

InP along with GaAs and GaP form a class of III-V semiconductor compounds that increasingly find new applications in the microwave and optoelectronics markets. GaP is exclusively used in the fabrication of visible light emitting diodes, while GaAs has found wide spread use in the fiber optic, optoelectronic, and microwave markets for military and commercial applications.

The publication in 1972 of ⁽¹⁾ a paper describing the InGaAsP/InP lattice matching properties along with the report that fiber properties of SiO₂ based optical fibers are optimized with respect to attenuation and dispersion in the 1.3-1.5 μ m range initiated a demand on InP. The demand however has been small and only recently devices based on InP are slowly emerging to the commercial scene. There are a number of reasons for the slow emergence of InP. Main ones are:

- a) InP to a great extent has similar properties to GaAs
- b) the areas that InP based devices outperform those based on GaAs such as fiber optic sources and detectors only recently are receiving widespread attention and
- c) the growth of bulk InP is plagued by severe technological problems, the most serious being the twinning problem when crystals are grown along the (100) direction.

B. Purpose of Research

At the beginning of this program the synthesis of high purity polycrystalline InP could be achieved only from In solutions in a horizontal Bridgman reactor ⁽²⁾. This is a very slow process and certainly not competitive with desired commercial development of InP. In addition, while almost all III-V compound device technology utilizes (100)

oriented wafers, reproducible single crystal growth of InP could only be achieved when pulled along the (111) direction.

This program addressed both of these limitations in the InP technology for the synthesis of high purity polycrystalline InP in the high pressure crystal puller and the growth of large (approximately 3.0") diameter (100) oriented InP single crystals.

II. InP Polycrystalline Growth

To date a number of techniques have been employed for the synthesis of polycrystalline InP to be used as feed-stock for single crystal growth. The most common being the horizontal Bridgman either from In solutions or at the stoichiometric point in high pressure autoclaves. Growth from solution is extremely slow, while the cost of high pressure horizontal Bridgman growers that can produce kilogram size charges are almost as expensive as high pressure crystal pullers.

Synthesis of GaAs in Czochralski crystal growers can be achieved by two drastically different processes a) reaction of the elements Ga and As encapsulated in B_2O_3 at the melting point of As (approximately $840^\circ C$) under high pressure (800-1000 psi) and b) injection of As to B_2O_3 encapsulated Ga at the melting point of GaAs ($1240^\circ C$) under relatively low pressures (standard Si and Cz growers have been employed for this process).

In the case of InP process (a) cannot be employed for two reasons 1) the vapor pressure of Phosphorus is quite high (1-3 bar) at the encapsulation temperature of $450-500^\circ C$ therefore excessive Phosphorus loss is expected prior to encapsulation and 2) the specific gravity of Phosphorus is quite close to that of B_2O_3 thus complete encapsulation might not be possible. The only alternative for synthesizing InP in the high pressure crystal puller is by injecting Phosphorus to B_2O_3 encapsulated Indium at the InP melting point under pressures greater than 27 bar. This process was first reported for the synthesis of GaP by Fisher⁽³⁾. Its application to InP was described by Wardill and co-workers⁽⁴⁾ and in a modified version for the in situ synthesis and growth of InP by Farge⁽⁵⁾. A variation of these approaches allowing controlled synthesis and subsequent single growth was reported by Hyder and Holloway⁽⁶⁾. The synthesis of

Phosphorus based compounds in the high pressure crystal puller however, is quite attractive for the following reasons:

- a) The elimination of expensive high pressure equipment for the synthesis of polycrystalline charges;
- b) The polycrystalline charges are crucible shaped therefore puller capacity for single crystal growth can be optimized.
- c) The eventual in situ single crystal growth.

The process developed at CrystaComm Inc. and described here is schematically shown in Figure 1. Indium and B_2O_3 are placed in a SiO_2 crucible in the susceptor of the resistance heated crystal puller shown in Figure 2. Phosphorus is placed in the ampoule and is suspended from the puller seed holder. The puller is sealed, evacuated and pressurized with either Ar or N_2 . Subsequently the Indium is heated to the InP melting point and is encapsulated by the B_2O_3 . Next the phosphorus ampoule is lowered until the injector penetrates the B_2O_3 and reaches the bottom of the crucible. The phosphorus is indirectly heated by the hot zone and is thus transported to the heated Indium. When the transport reaction is completed the ampoule is withdrawn and the charge is solidified. At present this process yields 1100 grams of fully stoichiometric large grain crucible shaped InP, as shown in Figure 3. The process duration is usually less than 3 hours with 1.5 hours heat up cycle, 30 minute reaction time, and 1 hour cooling cycle.

One of the primary goals of the program was to investigate the effect of the source of the starting material on the electrical properties of the synthesized polycrystalline InP. All electrical evaluation was done by Vander Pawe measurements at 300°K and 77°K. Since the polycrystalline growth process yields large, greater than 3cc crystallites all material evaluation was performed on single crystal wafers extracted from these crystallites. Table I lists the Indium,

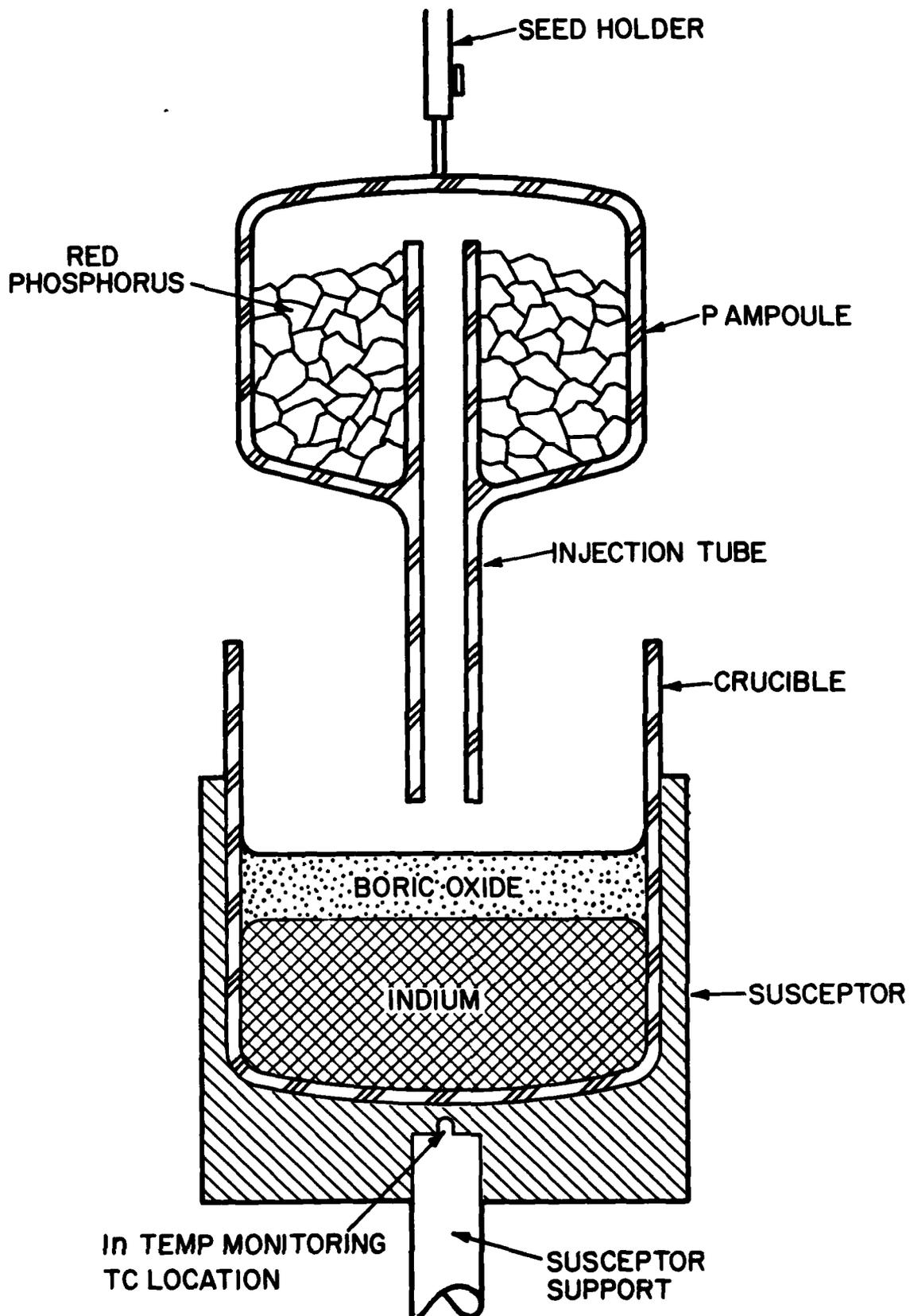


Fig. 1: Schematic representation of the injection of Phosphorus into B_2O_3 encapsulated Indium.

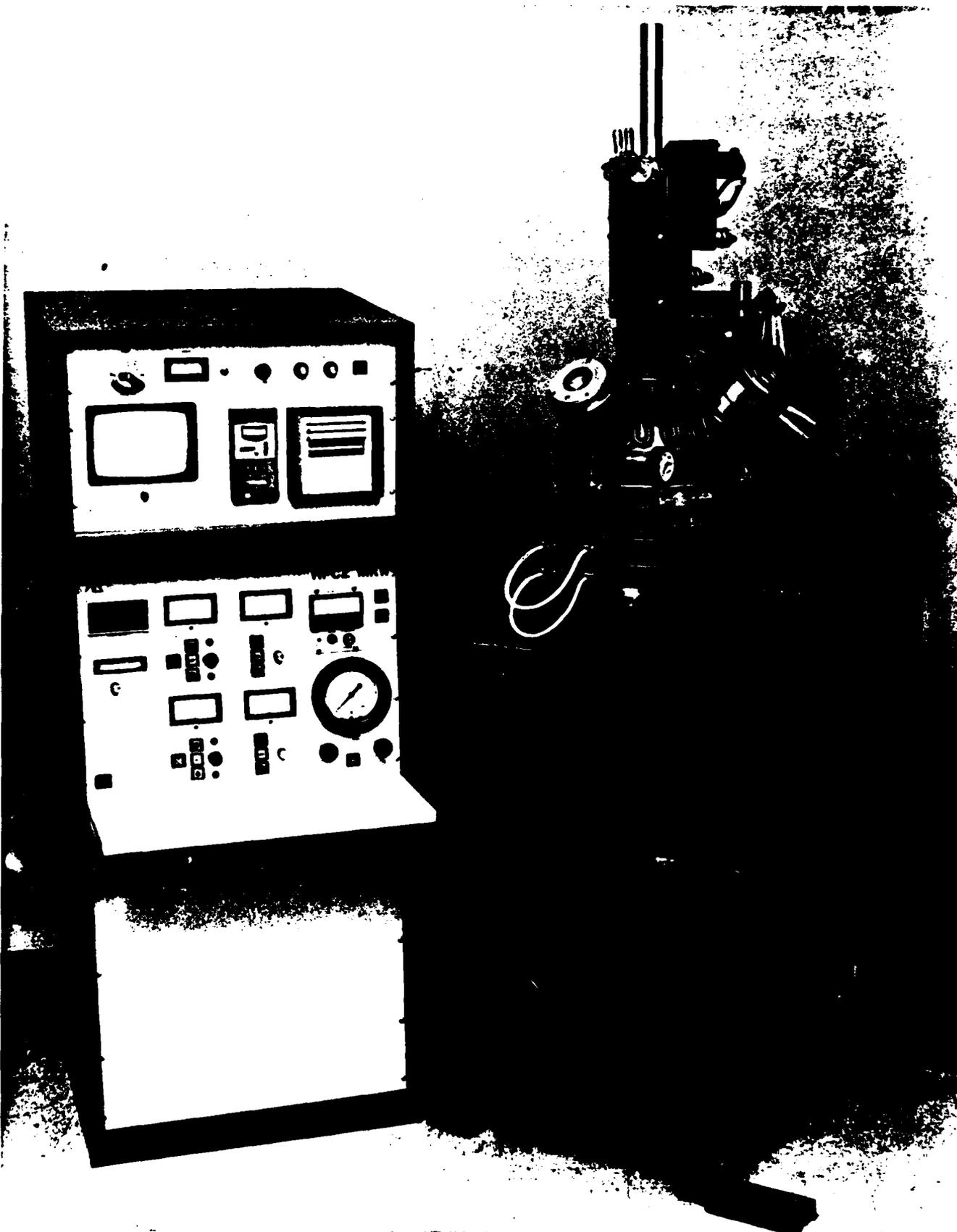
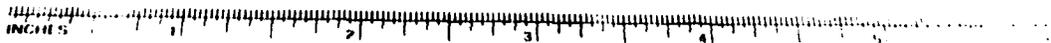
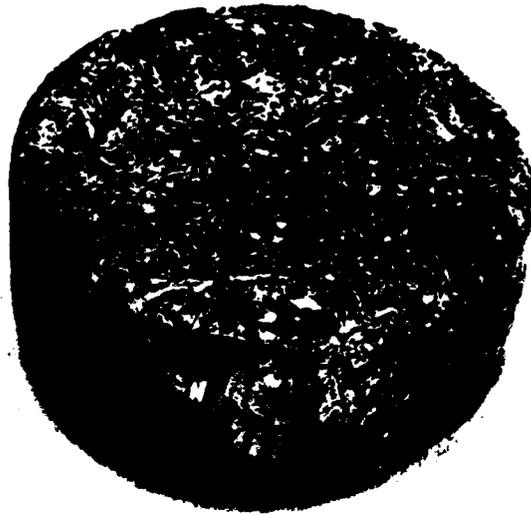


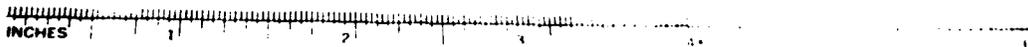
Fig. 2: A.D. Little high pressure crystal puller used in the growth of polycrystalline and single crystal InP.

a



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b



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Fig. 3: Fully stoichiometric, crucible shaped InP charge weighing 1100 grams.

a) top of ingot

b) bottom of ingot

(Spallation on top surface is caused when the B_2O_3 encapsulant is removed from the charge at room temperature.)

TABLE I: List of Materials Suppliers for the growth of polycrystalline InP.

<u>MATERIAL</u>		<u>SUPPLIER</u>	<u>GRADE</u>
In:	A	Mitsubishi	6'9
	B	Preussag	6'9
	C	J M C	A'1
P:	A	Mitsubishi	6'9
	B	Alussiuse	6'9
	C	Canyonlands	6'9
B ₂ O ₃ :	A	L.G. Williams	
	B	Rasa	H.P.
	C	Rasa	S.H.P.

Phosphide, and B_2O_3 commercial sources that supplies material for this study. Table II shows a summary of these results obtained from various source material permutations. While we have observed quality variation from batch to batch in material supplied by each manufacturer since we have made most extensive use of Indium supplied by Mitsubishi Corporation we have a higher confidence as to the reproducibility of the results using this source. In the case of Phosphorus and B_2O_3 our sampling indicated that basically material supplied by all manufacturers was comparable, disregarding of course B_2O_3 batches rejected from all manufacturers.

In order to assess the reproducibility of the process, we systematically evaluated the polycrystalline material reacted from Indium, Phosphide and B_2O_3 batches obtained from suppliers previously identified to supply the highest purity material. The results are shown in Table III. From this table we can observe that on the average the purity of the polycrystalline InP, obtained with starting source materials previously qualified as being of the highest purity is similar to that obtained with material supplied by practically all vendors. Since source materials were 6¹/₉ grade further improvements in purity of the polycrystalline material can only come about by painstaking assessment of the effect of the elemental purity and crucible material contribution to the background impurities.

TABLE II
Polycrystalline InP Characterization

	1	2	3	4	5	6	7	8	9	10
In Source	A	B	C	A	B	C	A	B	A	A
P Source	A	A	A	A	A	A	B	B	C	A
B ₂ O ₃ Source	A	A	A	B	B	B	B	B	B	C
$\frac{300^\circ\text{K}}{(N_D - N_A) \times 10^{15}} / \text{cc}$	2.46	4.00	4.20	3.20	4.07	2.20	3.40	3.40	3.89	1.90
$\mu (\text{cm}^2 / \text{v-sec})$	4480	3500	4020	4520	3910	4190	4230	4190	4140	4870
$\rho (\Omega\text{-cm})$	0.566	0.447	0.37	0.43	0.332	0.654	0.433	0.426	0.387	0.676
$\frac{77^\circ\text{K}}{(N_D - N_A) \times 10^{15}} / \text{cc}$	2.01	3.04	3.30	2.80	3.39	1.88	2.90	2.80	3.20	1.70
$\mu (\text{cm}^2 / \text{v-sec})$	25970	15800	18440	33490	27810	25990	33420	25690	24470	38040
$\rho (\Omega\text{-cm})$	0.12	0.13	0.102	0.067	0.066	0.127	0.063	0.087	0.08	0.096

TABLE III: Electrical characterization of polycrystalline InP using In, P and B₂O₃ sources considered to be the highest purity.

Run #	1186	1187	1188	1190	1197
300°K { (N _D -N _A)x10 ¹⁵ /cc	1.8	2.7	2.7	4.3	3.4
μ(cm ² /v-sec)	4220	4180	4620	4100	4280
@(Ω-cm)	0.82	0.55	0.75	0.35	0.42
77°K { (N _D -N _A)x10 ¹⁵ /cc	1.6	2.3	2.3	3.7	3.0
μ(cm ² /v-sec)	34040	28390	29240	26430	28230
@(Ω-cm)	0.118	0.095	0.092	0.085	0.074

III. Single Crystal Growth

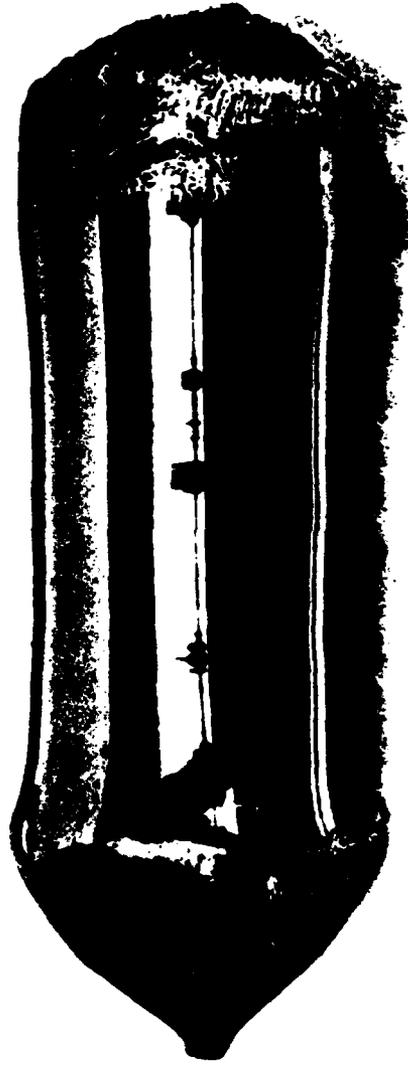
The growth of InP single crystals by the liquid encapsulation Czochralski process is plagued by severe twinning problems. There are reports in the literature that a) a minimum (unspecified) temperature gradient is necessary for the twin free growth of InP⁽⁷⁾, b) reduction of the viscosity of B₂O₃ by the addition of viscosity lowering agents, and as Ge₂O₂, Bi₂O₃, NaAlF, etc. improve single crystal yield⁽⁸⁾ and c) a minimum moisture content in B₂O₃ approximately 500ppm is necessary for elimination of twin formation⁽⁹⁾. The latter of course adversely affects the properties of the crystal since it has been shown that "grappe" formation is strongly dependent on the moisture content of the encapsulant⁽¹⁰⁾.

During the course of this program the growth of single crystal InP advanced from experimental (111) oriented 300 gm crystal, to the present 1100 gm, 7.5 cm diameter (100) oriented crystals that are routinely prepared on a production basis

The main breakthrough occurred in the design of a new hot zone for the growth of 400-500 gram (100) oriented crystals, that was later upgraded to the size that accommodates 1100 at present.

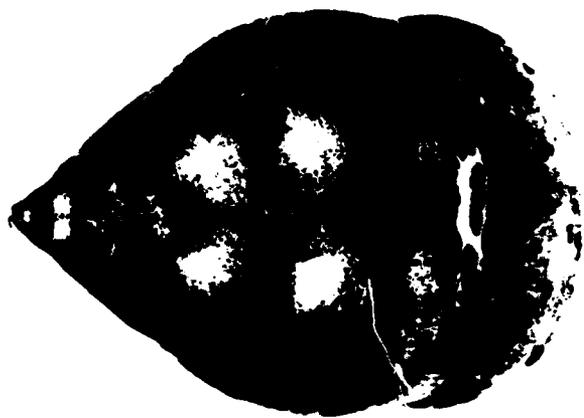
Figure 4 shows a 500 gram (100) oriented twin free InP crystal while Figure 5 shows a 1100 gram single crystal. The excellent diameter control evident in both figures is the result of the reproducibility of the thermal profile. The diameter is controlled automatically once the seeded crystal reaches a diameter of 2.0 cm. This is done strictly by controlling the cooling rate of the melt during growth. The optimum cooling rate evolved through numerous trial and error experiments.

Crystal characterization was performed by Vander Pawe measurements for electrical properties evaluation and by chemical etching and x-ray topography for defect characterization.



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Fig. 4: Zn doped twin-free InP single crystal grown along the (100) direction, 4 cm in diameter weighing 500 grams.



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Fig. 5: Fe doped twin-free (100) grown InP single crystal, 7.0 cm in diameter weighing 1 kg.

Growth of undoped InP single crystals using polycrystalline feedstock prepared by the injection of Phosphorus to B_2O_3 encapsulated Indium as described previously was performed at NRL in addition to a number of growths at CrystaComm. Typical results are shown on Table IV. It should be pointed out that these results are comparable on the average to the properties of the starting feedstock material.

Dislocation delineation was performed using the Huber etch⁽¹¹⁾. Figure 6 shows the dislocation density profile of a 70 mm diameter (100) oriented undoped InP single crystal. The EPD of 2×10^4 for the 5-6 cm center region is the lowest that has been reported for such large diameter crystals.

Seki et al⁽¹²⁾ have shown that impurity hardening by the addition of Zn or S to the InP lattice results in defect densities below $10^3/cm^2$ and zero defect densities have been obtained for moderate doping levels. We observed however that as the crystal diameter increased the doping concentration required for example in S doped crystals to maintaining constant defect density also increased. In qualitative terms a 5.0 cm (100) oriented crystal would require a Sulfur concentration of $4-6 \times 10^{18}$ in order to achieve a defect density less than $10^3/cm^2$. A 7.5 cm diameter Sulfur doped crystal would require $6-8 \times 10^{18}/cc$ concentration for the same defect density.

Similarly as the diameter increased from 5.0 to 7.5 cm the defect density of Fe doped, Sn and undoped crystal increased from $10^4/cm^2$ to $2-3 \times 10^4/cm^2$. This increase in defect density probably reflects the increased thermal stress that the crystal experiences during growth when the diameter of the crystal increases from 5.0 to 7.5 cm. Figures 6, 7, and 8 are transmission x-ray topographs (courtesy of RCA Corporation) of a Fe doped with $2-3 \times 10^4/cm^2$ EPD, and a Zn and S doped low EPD less than $10^3/cm^2$.

TABLE IV: Typical electrical properties of undoped InP single crystals prepared with CrystaComm polycrystalline InP feedstock.

	Crystal Grown at NRL Using CrystaComm InP Poly Charge	Crystal Grown at CrystaComm	
300°K {	$(N_D - N_A) / \text{cc}$	4.9×10^{15}	4.6×10^{15}
	$\mu (\text{cm}^2 / \text{v-sec})$	4255	4300
	$\rho (\Omega\text{-cm})$	0.298	0.314
77°K {	$(N_D - N_A) / \text{cc}$	4.2×10^{15}	3.75×10^{15}
	$\mu (\text{cm}^2 / \text{v-sec})$	28,163	23,680
	$\rho (\Omega\text{-cm})$.053	.070



Fig. 6: Projection x-ray topograph of an Fe doped high resistivity InP (100) oriented wafer indicating an EPD of $2 \times 10^4 / \text{cm}^2$.



Fig. 7: Projection x-ray topograph of a Zn doped (100) oriented wafer indicating practically zero defect density.

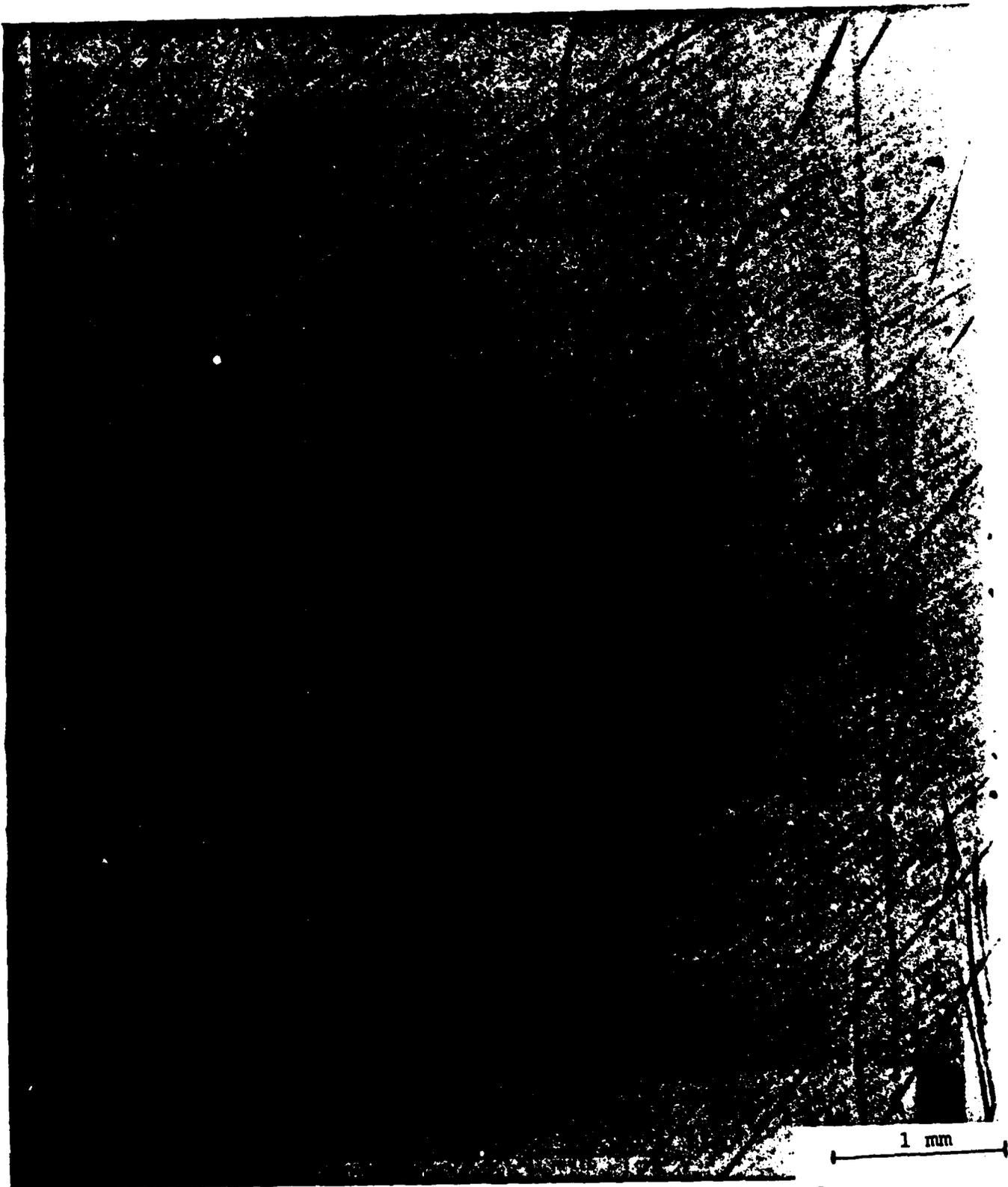


Fig. 8: Projection x-ray topograph of an S doped (100) oriented wafer indicating practically zero defect density.

IV. Summary

This three year program was instrumental in advancing the state of the art in InP growth. Processes have been developed for the rapid synthesis of high purity polycrystalline InP by the injection of phosphorus to B_2O_3 encapsulated indium in the high pressure crystal puller. Similarly processes have been developed for the growth of large diameter (7.5 cm) (100) oriented InP single crystals weighing more than 1100 grams.

Just as importantly, however, is that these processes have been scaled up once from 500 gram capacity to the present 1100 grams, and there is no obvious reason that they cannot be scaled up even further.

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