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RADC-TR-81-277
Final Technical Report
October 1981
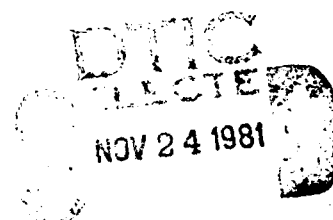
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HIGH-PRESSURE GRADIENT-FREEZE GROWTH OF SINGLE CRYSTALS OF INDIUM PHOSPHIDE

Crystal Specialties, Inc.

Worth P. Allred

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-81-277	2. GOVT ACCESSION NO. AD-A167731	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) HIGH-PRESSURE GRADIENT-FREEZE GROWTH OF SINGLE CYRSTALS OF INDIUM PHOSPHIDE		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 1 Apr 79 - 31 Dec 80
		6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) Worth P. Allred		8. CONTRACT OR GRANT NUMBER(s) F19628-79-C-0096
9. PERFORMING ORGANIZATION NAME AND ADDRESS Crystal Specialties, Inc. 419 W. Maple Ave. Monrovia CA 91016		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62702F 46001732
11. CONTROLLING OFFICE NAME AND ADDRESS Deputy for Electronic Technology (RADC/ESM) Hanscom AFB MA 01731		12. REPORT DATE October 1981
		13. NUMBER OF PAGES 28
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Same		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A

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)

Same

18. SUPPLEMENTARY NOTES

RADC Project Engineer: Joseph A. Adamski (ESM)

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

High Pressure Synthesis	III-V Semiconductor Compound
Indium Phosphide	
Phosphorous	
Stoichiometric Indium Phosphide	

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

A gradient-freeze growth system for the growth of large single crystals of InP is described. The system synthesizes and grows InP without reloading. Large poly ingots weighing up to 2,000 gms can be compounded by this method in a few hours. Ingots grown in the system have an impurity level of about 2×10^{16} atoms/cm^3. This technique promises to be a method by which large single crystals can be grown at a reasonable cost.

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SUMMARY

The objective of the work reported herein was to produce large single crystals of indium phosphide in a horizontal, gradient-freeze, high-pressure system using 2 mm- wall fused silica tubing to contain the growth boat and phosphorus over-pressure.

Since the partial pressure of phosphorus over InP at the melting temperature of the stoichiometric compound is approximately 27 atm, means had to be provided to prevent the thin-walled quartz tubing from rupturing. This problem was solved (1) in a prior contract (F19628-77-C-0105) by enclosing the quartz ampoule (and the furnace) inside a steel pressure vessel, and making use of a quartz bellows and a differential pressure transducer to sense the difference between the pressure inside the ampoule and that inside the pressure vessel. Means were provided to automatically reduce this pressure to zero.

One of the problems experienced on the prior contract was that convection currents in the nitrogen gas inside the pressure vessel were so extreme that it was not possible to maintain reasonable control of the temperature at the InP solid-liquid interface. To alleviate this difficulty a new pressure vessel was designed and built during the first months of the current program. The new vessel is much smaller than the one previously in use, so that convection currents have been reduced as much as possible.

Attempts were made to grow large single crystals of InP in a horizontal gradient-freeze system inside the pressure vessel. These runs were seeded with InP seeds cut from previously produced polycrystall ingots. Although none of these attempts were successful in producing large single crystals, it is apparent from the results that single crystals could be produced if two problems were resolved. The problems are (a) boat wetting and (b) oxides floating on the surface of the melt.

The system allows in situ reaction of the starting elements immediately prior to growth, and it was established that large (>600 gms) charges could be brought to temperature, reacted and stabilized with respect to temperature and pressure in less than three hours.

Large, dense, polycrystalline boules of stoichiometric InP were produced easily in the latter stages of the work.

The synthesis and growth system, including the apparatus used to maintain the differential pressure between the ampoule and the pressure vessel at zero, is described in Section 2 of this report. The synthesis and growth techniques are discussed in Section 3, and results are presented in Section 4.

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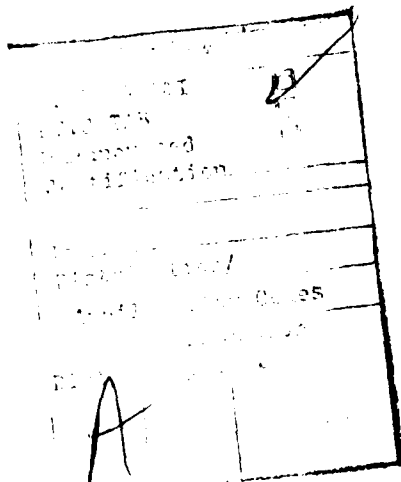
PREFACE

This report describes research and development efforts on an internally pressure-balanced method of growing crystals of indium phosphide. The program was the second phase of an effort sponsored by the Deputy for Electronic Technology (RADC), Hanscom Air Force Base, MA.

Most of the effort on the first phase was devoted to the design and construction of the growth and pressure balancing systems and to preliminary InP synthesis and growth runs to evaluate the apparatus and the method. That work was reported on in the Final Technical Report on Contract No. F19628-77-C-0105(1).

Modifications to the apparatus, based on the findings in the first phase of the work, are described in this report. Large (>600 gms) dense polycrystalline ingots of stoichiometric InP can now be easily produced. However, the growth of single crystals has been severely hindered by the presence of oxides floating on the melt.

Some of the work reported herein was discussed in a paper given by W. P. Allred, J. W. Burns, and W. L. Hunter (2) at the 1980 NATO Sponsored InP Workshop held in June, 1980 at Harwichport, MA. The Workshop, the proceedings of which are to be published in a special issue of the Journal of Crystal Growth, was chaired by John K. Kennedy, the RADC/ET Project Scientist on this program.

Worth P. Allred was the Principal Investigator on the

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1. INTRODUCTION

Several methods of growing single crystals of indium phosphide were evolved earlier by other workers. These methods include growth from dilute solution (3); growth through vapor phase chemical reactions (4); high-pressure horizontal gradient-freeze systems (5, 6); and high-pressure liquid encapsulated (LEC) Czochralski pulling (7). Of these, only the last two methods have yielded relatively large single crystals in reasonably short growth times, and it should be noted that both methods involve the use of high pressures.

Crystals of InP grown previously by the high-pressure, gradient-freeze technique were grown in small-diameter, thick-walled quartz tubing. The tubes were 10 mm ID and had a wall thickness of 3 mm. The strength of the tubing was sufficient to hold the 27.5 atm pressure (6) of phosphorus generated at the melting temperature of stoichiometric InP, 1062°C, but the crystals, although satisfactory, were not large enough to meet the needs of today's device technology.

Larger crystals of InP have been pulled by the liquid-encapsulated Czochralski technique, in which a layer of boron oxide is floated on the surface of the melt to prevent the escape of phosphorus. One major disadvantage of this method is the difficulty of reacting indium and phosphorus under the B_2O_3, making it necessary to use the prereacted compound as the starting material. Another disadvantage is that a layer of B_2O_3 adheres to the InP crystal and generates stresses in the

crystal as it cools.

The approach adopted in the work reported herein was designed to obviate the difficulties inherent in the afore-mentioned processes. Thus, the growth ampoule is 57 mm ID and only 2 mm in wall thickness, permitting the growth of large-cross-section crystals in ordinary fused quartz tubing. The use of a horizontal gradient-freeze system permits the in situ reaction of the indium and phosphorus immediately prior to growth.

The gradient-freeze crystal grower is housed in a steel high-pressure vessel. The indium is contained in a fused quartz boat, which is placed in the fused quartz ampoule together with the amount of phosphorus needed to produce a stoichiometric melt and also maintain the necessary phosphourus pressure. The elements are reacted in the ampoule prior to growth, and as the phosphorus pressure inside the ampoule increases during heating, the pressure of an inert gas, nitrogen, outside the ampoule (and inside the pressure vessel) increases correspondingly, so that equal pressures are maintained within and without the quartz ampoule, thus preventing explosions. The method of controlling the differential pressure and reducing it to zero are described in the following section of this report.

It was mentioned in the Summary that a decision was made late in the previous contract to build a smaller pressure vessel in order to minimize convection currents. Building this system required more than six months at the beginning of this

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contract. After this system was completed, polycrystalline ingots of InP weighing several hundred grams were produced. None of the runs yielded completely single crystals. The reasons for this are discussed in Section 4.

2. SYNTHESIS AND GROWTH SYSTEM

A new steel pressure vessel, measuring 7'4" in length and 9-3/4" internal diameter, was designed and built during the first phase of the program. Copper tubing, 3/8" ID, was coiled and welded to the outside of the vessel to permit water cooling. A three-zone, resistance-heated, gradient-freeze furnace was mounted inside the pressure vessel, as shown in Fig. 1. Separate temperature controllers were provided for each of the three zones, and a Data Trak programmer was utilized to permit the gradual programmed decrease of temperature with time in both the hot zone and the growth zone. The phosphorus control zone temperature was not programmed.

Due to the high pressure of phosphorus over stoichiometric InP at its melting point, it is necessary to equalize the pressure on the quartz ampoule to prevent explosions. The system is so designed that the differential pressure between the synthesis ampoule and the inside of the pressure vessel is near zero. As the phosphorus pressure increases on heating, a quartz bellows, which forms one end of the ampoule, expands. This produces a movement of a quartz rod that is attached to

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the bellows. Referring to Figs. 1 and 2, a transducer which is located at the end of the quartz rod, and which is referenced by a quartz tube fastened at the front of the bellows, senses the motion of the rod.

The transducer generates a voltage which is proportional to the increase in phosphorus pressure. This voltage is fed to a signal amplifier and conditioner, which modifies the signal for use in a servo system. The servo amplifier signals a motorized regulator which adds nitrogen gas to (or releases it from) the pressure vessel, according to the sign and magnitude of the differential pressure sensed by the transducer.

Differential pressures as low as 0.1 lb. per sq. in. can be sensed by this technique, so the apparatus makes it feasible to react charges as large as 2000 gms, with pressures of 27 atm, in ordinary thin-walled quartz tubing, with no danger of explosion.

An emergency vent valve is also controlled by the servo system. This vent valve is activated when a positive differential pressure (excess pressure on the outside of the ampoule) exceeds some preset value. This value is adjustable from 1.0 to 50 lbs/in^2. The emergency vent provides protection for the ampoule in the event of a sudden temperature drop caused by a furnace or power failure.

3. SYNTHESIS AND GROWTH TECHNIQUE

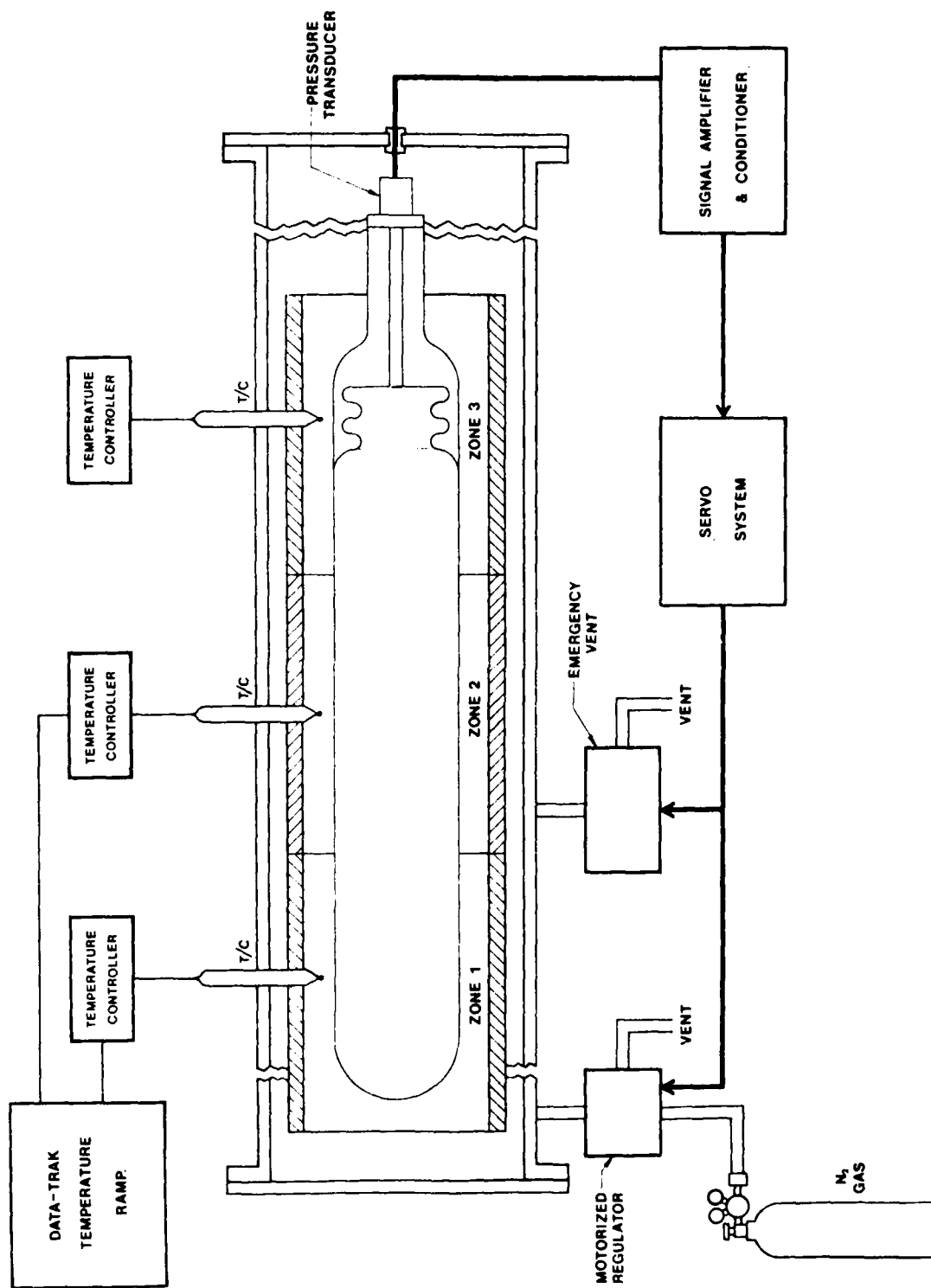Six-nines-pure red phosphorus is placed at the bellows

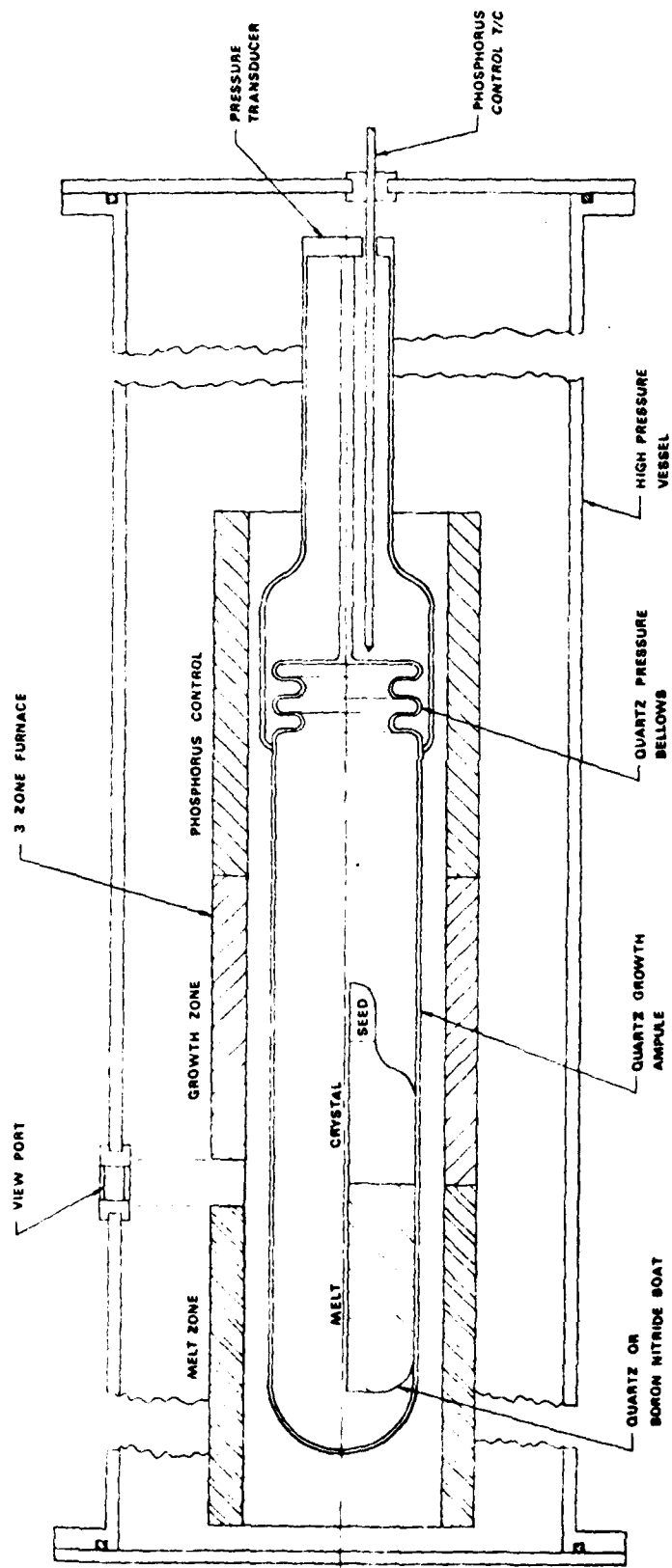Fig. 1. High-Pressure, Gradient-Freeze, Growth System

Fig. 2. Arrangement of Boat and Pressure Bellows

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end of the ampoule. Six-nines-pure indium is loaded into the growth boat, which is then slid into the ampoule and positioned near the end away from the bellows. A short (two-inch) piece of quartz tubing, closed on one end, is slid into the ampoule after the boat.

The tubing used for the ampoule was usually 57 mm ID by 61 mm OD. The short piece of tubing, or plug, inserted into the ampoule after the boat, had an OD of 55 mm, and was used for sealing the ampoule after evacuation. The evacuation was by means of a cryopump, and the ampoules were pumped out to 10^{-6} Torr. During pump-down with the cryopump, the indium was vacuum heat-treated, usually for two hours, with a resistance-heated tube furnace at 800°C. In the later stages of the program, the indium was heat-treated in hydrogen prior to loading in the growth ampoule. The purpose of this was to reduce oxides floating on the surface of the indium, but oxides were never completely removed, and remained a problem throughout the program.

In addition to the phosphorus required to produce a stoichiometric melt, excess phosphorus was added to the ampoule to maintain the phosphorus pressure. It was found experimentally that, for the ampoule volume used, 75 to 80 gms of excess phosphorus were required.

The ampoule was sealed by shrinking and fusing a short section of it to the quartz plug, after which it was loaded into the furnace within the pressure vessel. The latter was then

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closed, and the temperature of zones 1 and 2 was quickly brought to the melting temperature of InP, 1062°C. At the same time, the temperature of the phosphorus zone was brought to 750°C. At these temperatures, all of the phosphorus was either in the melt or in the vapor state.

During the reaction to form InP, the pressure control servo system automatically adjusted the nitrogen pressure in the vessel to that of the phosphorus in the ampoule, thus maintaining the differential pressure near zero. Near completion of the reaction the pressure in the system was observed to rise above the equilibrium dissociation pressure, to approximately 450 lbs/in.^{2} As the reaction then proceeded, the pressure dropped to the value given by Bachmann (6), 397 lbs/in.^{2}

Some problems were encountered in achieving proper bellows fabrication techniques, and in the operation of the pressure control servo system. As a result, some of the runs ended in explosion or implosion of the ampoule. The pressure control system was modified to include a proportioning type pulsating value control which opens either the inlet or outlet valve for a time period which is proportional to the differential pressure. This modification, together with improved bellows fabrication methods, has resulted in a system which has proven to be a reliable apparatus for containing molten compounds with high vapor pressures in thin-walled quartz tubing. Stoichiometric InP melts weighing up to 1000 gms can be synthesized in three hours.

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Attempts were made to grow single crystals of InP after the synthesis reactions were completed. The melt was brought in contact with a seed crystal in the spoon of the boat by raising the tail end of the pressure vessel. The temperatures in the three furnace zones were controlled by independent temperature controllers, and a temperature profile sloping from 1060°C to approximately 1100°C was established along the length of the boat. The phosphorus control zone was set at 750°C. A Data Trak program unit, manufactured by Research, Inc., was programmed to reduce the temperatures in zones 1 and 2 at a slow rate, while maintaining the temperature gradient, so that the melt froze slowly from the seed end.

Growth of the crystal was observed through viewports in the top of the furnace and pressure vessel. The experimental results are discussed in the following section.

4. EXPERIMENTAL RESULTS

Problems with the new growth system resulted in the failure of the first three runs, two of which resulted in explosions. One run was aborted because of a nitrogen gas leak in the system. The positioning of the thermocouples caused the ceramic protection tubes to be broken in shear due to thermal expansion of the furnace. This caused intermittent shorting of the thermocouples. A second problem with the thermocouple placement was that they were passed through the wall of the

pressure vessel and held in place by O-ring seals. In fact, however, these seals failed to hold the thermocouples. The latter were forced back out through the seals to the outside of the pressure vessel as the nitrogen pressure inside increased. The thermocouples were repositioned so as to be entirely within the pressure vessel, with only the extension wires passing through the wall. The extension wires were epoxied into steel plugs in the wall of the pressure tank. This solved the thermocouple problem.

Run No. 130 was made with a charge of 282.50 gms of In, 76.19 gms of P, and an excess of 55.00 gms of P to establish and maintain the necessary partial pressure of P over the melt. The charge was vacuum heat-treated after evacuating to 2×10^{-6} Torr with the cryopump. Prior to seal off, the ampoule was backfilled with nitrogen to a pressure of approximately 1.0 psi.

The indium in this run was brought to a temperature of $1086^{\circ}C$ within one hour after turning on the furnace power. At the same time, the temperature in the phosphorus control zone was raised to $570^{\circ}C$. The charge was allowed to react and soak for four hours after these temperatures were reached. A temperature profile sloping from approximately $1060^{\circ}C$ to $1100^{\circ}C$ was then established along the length of the boat. The phosphorus control zone was set at $750^{\circ}C$, and the pressure readout settled at 340 psi, or approximately 23 atm. The Data Trak was programmed to cool the hot zones at a rate of $5^{\circ}C$ per hour for twenty hours, and the charge was then cooled through the freezing

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point automatically.

Most of the resulting ingot, which had been seeded with an indium phosphide seed oriented in the [111] direction, was In-rich and polycrystalline, but the top section near the tail was large-grained and dense enough to permit a Van der Pauw evaluation of the electronic properties. The $300^{\circ}K$ results gave a resistivity of 9.3×10^{-2} ohm-cm, $2800\ cm^2/volt$ sec for the mobility, and a carrier concentration of $2.3 \times 10^{16}/cm.^3$

Run No. 131 was very similar to No. 130. The same amounts of In and P were used for the charge, and the same mass of excess phosphorus was loaded into the ampoule to maintain the phosphorus pressure. As before, an InP seed was used, again in the [111] direction. This run was heated more slowly, however, and the melt was allowed to soak for approximately twelve hours before any cooling took place. The visibility of the melt through the viewports was quite good. At one point dendrites were observed growing on the surface prior to the initiation of the cooling program, necessitating an increase in the temperature settings. This run was cooled at a rate of $7^{\circ}C$ per hour for fifteen hours. Prior to cooling, the temperature of the phosphorus control zone was set at $770^{\circ}C$, somewhat higher than the $750^{\circ}C$ of Run No. 130, and the pressure also increased to 360 psi.

The results of Run No. 131 were comparable to No. 130. The ingot was In-rich and polycrystalline, the tail end being quite porous.

The next run loaded into the high-pressure system was

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No. 133. (No. 132 was not loaded because of a poor vacuum seal.) The charge was increased in No. 133, to 338.9 gms of In and 91.40 gms of P. Additionally, the excess phosphorus was increased to 70.0 gms from 55.0 gms.

This run was heated and fully reacted in one hour fifteen minutes. It was allowed to soak for four hours, after which it was cooled at a rate of 10°C per hour. Observation of the melt surface indicated that this crystal grew at a rate of approximately 1/2" per hour. The pressure at the beginning of the programmed cooling was 400 psi, with the phosphorus control temperature at 700°C. After eight hours cooling, the surface of the ingot was completely solid. Two hours later, the power was shut off, at which time the phosphorus pressure was 360 psi.

This was easily the best run up to that point in the work. The entire boule was dense and stoichiometric except for the tail, which was In-rich. The front third of the ingot showed strong faceting on the bottom, although it was polycrystalline. The grain size in the bulk of the ingot at the front end was larger than on the top surface. The top was characterized by a fine-grained structure indicative of either an oxide floating on the surface or an impurity segregating to the front. The grain size in the middle section of the ingot was considerably larger than at the front, and the fine structure disappeared from the top surface.

In the next run, No. 134, a five-inch long, half-round quartz boat was used. The charge consisted of 294.00 grams of

pure indium, 79.29 grams of phosphorus, plus an additional 70

grams of phosphorus to maintain the phosphorus overpressure

in the ampoule. After reacting and soaking for four hours the

system was programmed to cool at a rate of $2^{o}C$ per hour. This

was considerably less than the 5° to $10^{o}C$ per hour cooling rates

used in previous runs. The objective was to determine if the

slower rate resulted in single crystal growth, or larger grain

growth. It did not, the results being comparable to those of

Run No. 133. The phosphorus pressure at the start of programmed

cooling in Run 134 was the same as in Run 133, namely 400 psi.

The next two runs were comparable to No. 134, but in Run

135 the cooling rate was $6^{o}C$ per hour, and in Run 136 it was

$3^{o}C$ per hour. Problems encountered in subsequent runs necessi-

tated the installation of the proportioning type pulsating

valve control on the pressure control system. The bellows design

was also modified.

The last two runs made during the program yielded results

comparable to those of earlier runs. Although dense, stoichio-

metric, polycrystalline InP can now be prepared quite easily and

rapidly, it has not yet been possible to grow a boule which is

entirely single crystal.

The principal problem impeding the growth of single

crystals is an oxide layer floating on the surface of the melt.

Convection currents in the melt cause the oxide film to move to

the cooler, seed end of the boat. This has made it impossible

to maintain single crystal growth off the seed. The presence

of the oxide film at the front also explains the fine-grained structure on the top surfaces of the ingots near the front ends.

The electronic properties of several of the crystals were measured. The room-temperature mobilities were in the range from 2500 to 3300 cm^2/volt-sec, with carrier concentrations in the low-to-mid 10^{16}/cm^3 range. All of the material was n-type as grown. The highest mobility observed at 77°K was 19,000 cm^2/volt-sec.

5. CONCLUSIONS

An internally pressure-balanced system making use of a three-zone gradient-freeze furnace for the growth of InP has been successfully developed. The system employs a quartz bellows at one end of the growth ampoule, a differential pressure transducer, and a servo system to control the nitrogen pressure in the pressure vessel which encloses the ampoule. The nitrogen pressure in the vessel is automatically adjusted so as to equal the phosphorus pressure in the ampoule, thus eliminating the problem of ampoule explosions.

Large melts of InP can be reacted rapidly in this system, and growth of crystals can proceed after the reaction of the starting elements is complete, without cooling or opening the system. Thus it is not necessary to use pre-reacted InP as the starting material in the process.

Although all of the ingots grown during the program were

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polycrystalline, it is clear that the system and the technique would yield single crystals of InP if the problem of oxides floating on the melt surface could be solved. It was noted that the InP grain size was always larger at the middle and tail of the ingot than at the front. The smallest grains were always at the top surface on the front end. This is the result of the oxides on the surface being carried to the front end by convection currents in the melt. These oxides prevented single crystal growth off the seed, and resulted in a fine-grained structure on the top surface of the ingot near the seed.

Extensive impurity measurements have not been made, but Van der Pauw data on wafers from some of the ingots show the residual impurity concentration to be in the low $10^{16}/cm^3$ range.

6. RECOMMENDATIONS

The major problem is the film of oxide floating on the InP melt. Since convection currents cause this oxide layer to move to the front of the melt, where it contacts the seed crystal, it has been impossible to grow single crystals. The oxide provides nucleation sites for many new grains. It is recommended that extensive heat-treating of the indium in hydrogen, after final loading of the ampoule, be conducted in an attempt to reduce these oxides. If this, or any other method, were to succeed, there is very good reason to believe that large single crystals of InP could be grown.

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