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DEVELOPMENT OF TECHNIQUES FOR THE GROWTH OF BULK SINGLE CRYSTALS OF SEVERAL III-V COMPOUND SEMICONDUCTORS

by

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JOHN S. HAGGERTY and JOSEPH F. WENCKUS

JUNE 1970

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FINAL TECHNICAL REPORT

Prepared under

Contract No. NAS 12-2020

by

ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASSACHUSETTS

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I. SUMMARY

Under sponsorship of NASA/ERC, techniques sufficiently compatible as to be usable in a commercial single crystal growth apparatus have been developed to produce high-quality single crystals of GaAs, InAs, GaP, InP, GaSb, and InSb. These techniques were used successfully for all of these materials with the exception of InP. Single crystals of InP could not be grown from commercially available raw materials, which were phosphorus-deficient.

The liquid-encapsulated Czochralski crystal growth process was used both to suppress the loss of volatile components from the melts and to dissolve non-volatile films from their surfaces. High-purity B_2O_3 was used as an encapsulant, and ambient furnace gas pressures ranged from 3 psig for InAs to 800 psig for GaP.

Crystals of all of these materials have been grown with equivalent or higher purities than the starting materials using the B_2O_3 encapsulated growth process. There appears to be little contamination of the melts by the encapsulant or the crucibles. Single crystals of GaAs, GaP, and InSb with carrier concentrations below 10^{16} per cm^3 were reproducibly grown. GaAs crystals with carrier concentrations as low as 10^7 per cm^3 and GaP samples as low as 10^3 per cm^3 were also grown, but they were undoubtedly compensated. Comparisons of the carrier concentrations in the feed materials with those in the crystals show that there is little segregation of the electrically dominant impurities in InAs, InP, and GaSb during solidification. Achieving the desired carrier concentration (below 10^{16} per cm^3) in these crystals will require the use of purer feed materials.

Electron and hole mobilities observed in these crystals show that good quality crystals of all of the compounds investigated can be produced by the liquid-encapsulated Czochralski technique.

GaAs crystals up to 2-1/2 inches in diameter were produced. The maximum diameters of crystals that can be produced by this process are limited only by the same factors which set the upper diameter limits in normal Czochralski growth.

Compounds with highly volatile constituents can be synthesized under a B_2O_3 encapsulant. Stoichiometric GaAs and phosphorus-deficient GaP melts were synthesized by this technique. The B_2O_3 remained sufficiently clear to initiate Czochralski growth without handling the melt further.

The procedures used for growing single crystals of these six compounds are presented in sufficient detail that they may be reproduced in other laboratories.

II. INTRODUCTION

Commercial and technical interest is increasing in the III-V class of intermetallic compounds for use in solid-state devices, particularly GaAs, GaP, and their mixtures for light-emitting diode applications. Numerous devices based on single crystals of these compounds have been produced on a laboratory scale, and many will be produced at full production levels in the near future. Even though the properties of many of the pure, mixed, and doped compounds have appeared in the technical literature, single crystals with tailored properties have generally not been available to researchers. There is also an obvious need for advancing the state of the art of processing technology to make growth of large single crystals feasible. This program was carried out from June 1968 to June 1970 (experimental work carried out only during the first 18-month period) with the objective of satisfying these needs for NASA/ERC.

The partial pressure of one of the elements of many of the III-V compounds at their melting points is sufficiently high that special growth techniques must be employed to prevent excessive deviations from the desired stoichiometry or dopant levels. Vapor pressures range from 1/3 atm of arsenic in equilibrium with an InAs melt at 942°C to 35 atm of phosphorus in equilibrium with a GaP melt at 1450°C.

Traditionally, the loss of volatile constituents has been controlled by either lowering the equilibrium vapor pressure or maintaining the equilibrium atmosphere over the melt. The vapor pressure can be lowered by growing at low temperatures from saturated solutions. This type of growth is characterized by slow growth rates, entrapped solvent, and small, randomly nucleated crystals. The hot-wall autoclaves that maintain equilibrium atmospheres over the melts are typically complex and unreliable. Their use is limited in practice to the arsenides, since there are no materials which can support the stress levels at temperatures required for the phosphides without contaminating the melts

excessively. It is the inherent complexity of the hot-wall apparatus that has limited the size of the III-V single crystals grown by the Czochralski technique.

Metz et al.[1] described an approach to controlling the vapor losses from contained melts which is basically different from those discussed above. They used a liquid encapsulation technique, shown schematically in Figure 1, for growth of PbSe and PbTe single crystals. In this method, the vaporization rate from the compound melt is reduced by the presence of a nonreactive, low-vapor-pressure liquid encapsulant. If the ambient gas pressure is higher than the vapor pressure of the melt, nucleation of vapor bubbles is prevented and the vaporization loss is limited to that which occurs by diffusion through the liquid encapsulant. The encapsulant must be less dense than the molten compound, transparent, chemically inert, and have a low solubility in the compound.

Mullen et al.[2] reported the use of this method for the growth of InAs and GaAs from stoichiometric melts. A variety of encapsulants were used, and B_2O_3 was found to be the best material to encapsulate those two arsenides. Very little boron contamination of the III-V melts occurs from the B_2O_3. The liquid B_2O_3 was reported to act as a getter for foreign metallic oxides from the melts[3] and to effectively remove trace oxide impurities from the surface of the charge before it melts.[2]

The principal advantage of the liquid encapsulation technique in the growth of high-vapor-pressure, high-melting-point compounds is that the high-temperature region of the crystal growing furnace can be confined to the melt and crucible. The cooled walls of the containing jacket need only withstand an inert gas pressure equal to the dissociation pressure of the most volatile constituent, and the walls of the pressurized container do not come in contact with the corrosive arsenic or phosphorus vapors.

The liquid encapsulation technique has been used successfully throughout this program, both to control vapor losses and to clean melt surfaces of oxide films.

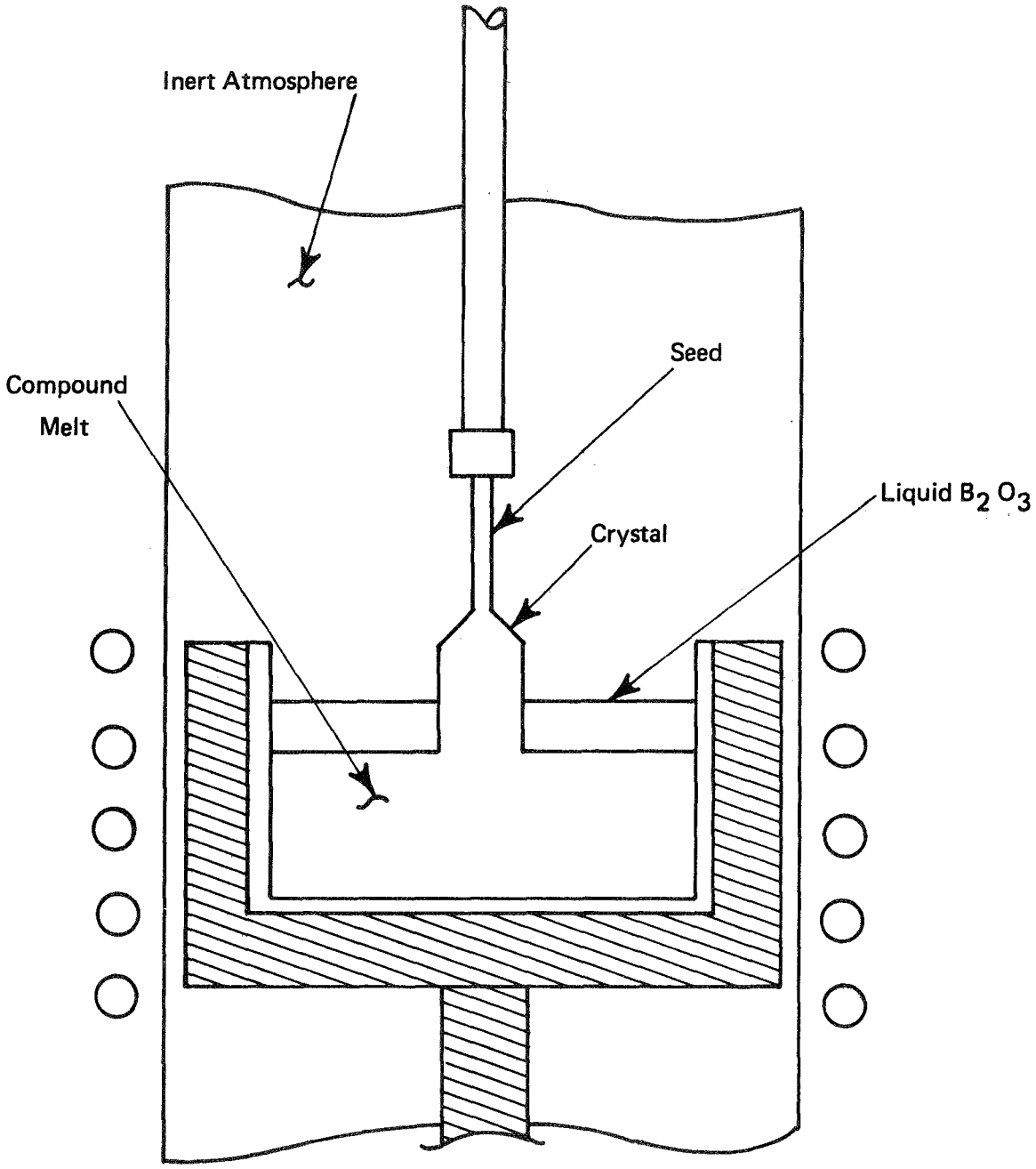

FIGURE 1 LIQUID-ENCAPSULATION TECHNIQUE

The objectives of this program have been to (a) grow single crystals of GaAs, InAs, GaP, InP, GaSb, and InSb and to relate the growth parameters to the properties of fully characterized crystals with the goal of achieving carrier concentration levels below 10^{16} per cm^3, (b) develop procedures to synthesize the high-vapor-pressure compounds under an encapsulant from condensed-phase constituent elements, (c) supply single crystals to NASA/ERC for internal and sponsored research programs, and (d) document the growth procedures in sufficient detail to permit reproduction in other laboratories.

On the basis of a program plan formulated during discussions with the contract monitor, single-crystal growth experiments have been made with GaAs, InAs, GaP, InP, GaSb, and InSb during this program. High-purity single crystals of all the compounds have been produced with the exception of InP; all InP boules grown were polycrystalline. Synthesis experiments were made with GaSb, InSb, GaAs, and GaP. The procedures used for each compound differ and are discussed in detail in the following sections.

III. TECHNIQUES AND APPARATUS

A. CRYSTAL GROWTH APPARATUS

Crystal growth experiments undertaken during the program were made by solidifying directly from stoichiometric melts using the Czochralski and vertical Bridgman modes of growth. The Czochralski growth technique is nearly optimal with respect to crystallographic quality, ease of seeding, relatively rapid growth rate, and size of crystals that can be grown. The Bridgman technique permits long-duration, slow-growth-rate runs to be made with a minimum of supervision.

Gallium and indium antimonides have been grown both with and without liquid (B_2O_3) encapsulants, since the vapor pressures in equilibrium with these stoichiometric antimonide melts are sufficiently low that the melts do not shift from their stoichiometric compositions during the crystal growth process. Non-volatile, solid films form on both melts if the furnace atmosphere and charge are not free of oxygen. The B_2O_3 encapsulant proved useful in dissolving the oxide films from the surfaces of the melts, making the growth of single crystals possible. The gallium and indium arsenides and phosphides were melted under a B_2O_3 encapsulant to suppress the loss of arsenic and phosphorus from the melts. Operating furnace atmosphere pressures during crystal growth ranged from 3 psig for InAs up to 800 psig for GaP. Pressures up to 1250 psig were employed during synthesis experiments.

The crystal growth experiments were carried out in two crystal growing furnaces available at ADL. The antimonides and arsenides were grown in a standard Model MP furnace (Figure 2), which has a maximum operating pressure of 300 psig; the phosphides were grown in a prototype high-pressure Model HP furnace (Figure 3), which can be operated at pressures up to 1250 psig. Despite the relatively large number of growth experiments scheduled in the standard MP furnace, no antimonide and few arsenide growth experiments were made in the HP furnace to avoid possible contamination.

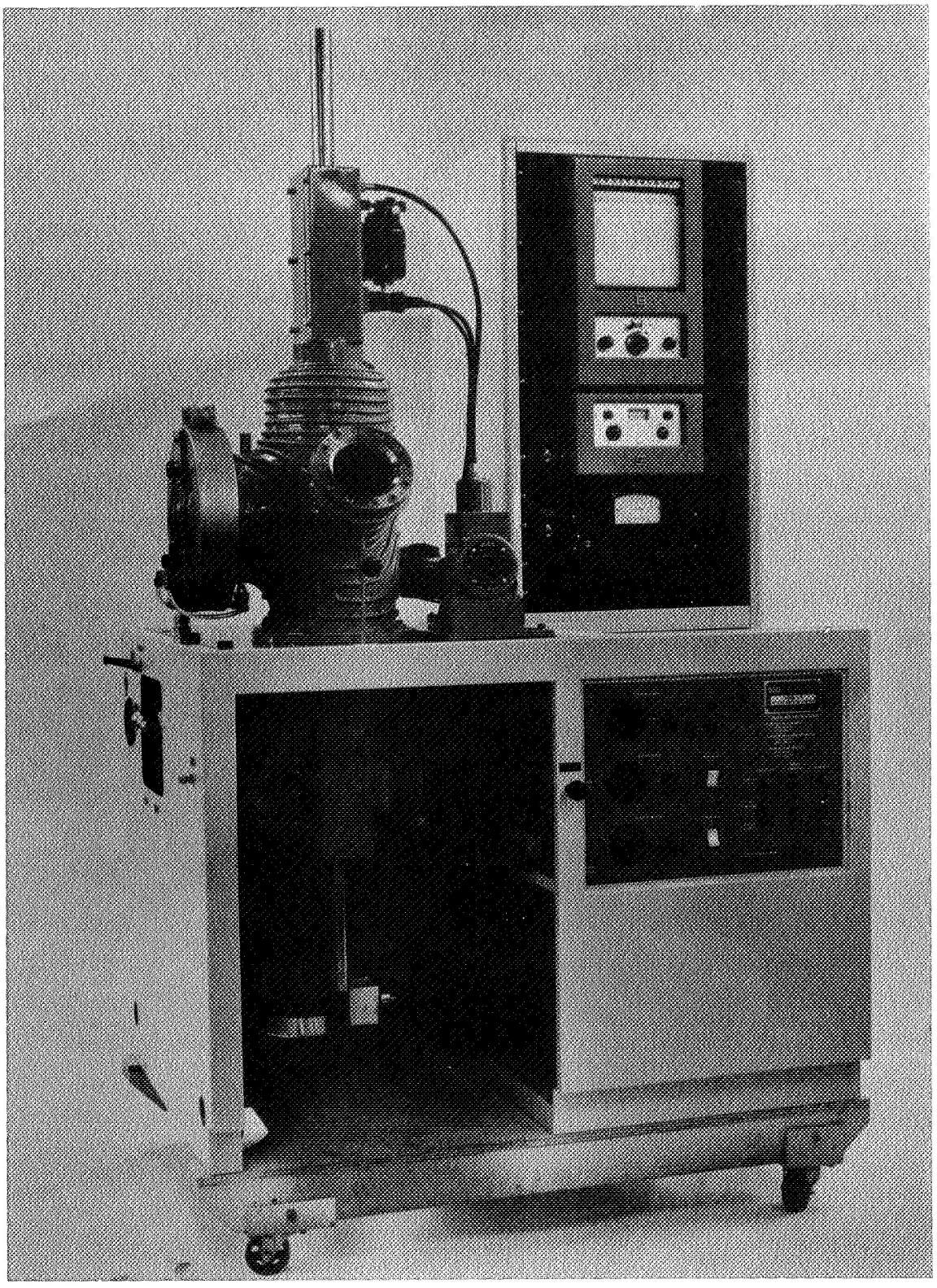

FIGURE 2 ARTHUR D. LITTLE MODEL MP CRYSTAL GROWING FURNACE

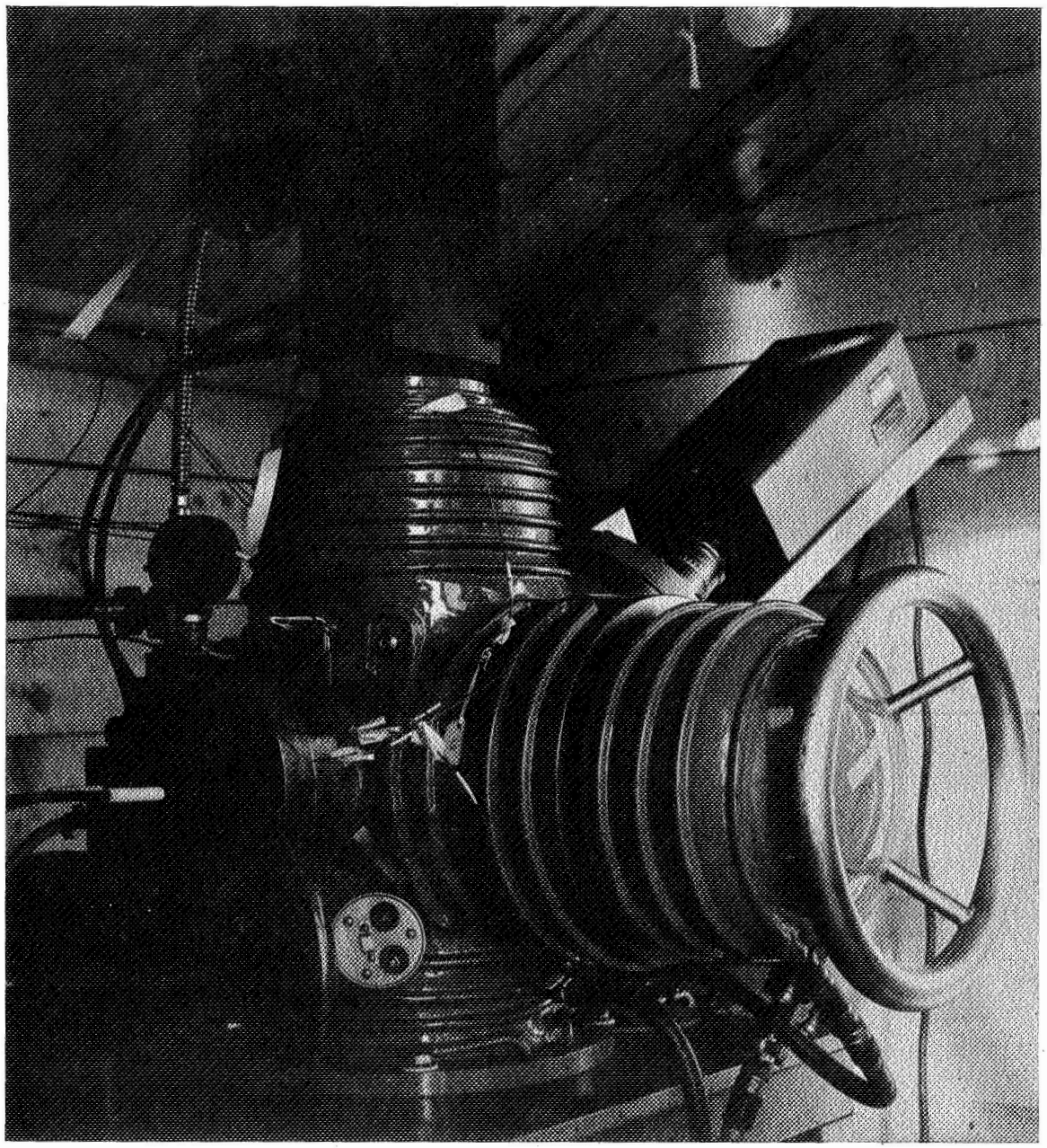

FIGURE 3 ARTHUR D. LITTLE HIGH PRESSURE MULTIPURPOSE CRYSTAL GROWING FURNACE

The standard Model MP furnace can be operated in laboratories at pressures up to 300 psig without providing special protective enclosures for the furnace. Even though the chamber of the Model HP furnace is ASME code-approved for operation at pressures up to 1500 psig, it is suggested that at pressures above 300 psig it should be operated remotely in a cell that is adequate to protect personnel if a failure should occur. The growth process was monitored primarily by means of closed-circuit television. The degree of visibility attained with this system is shown in Figure 4.

The rf power supplies for both furnace systems were controlled by saturable core reactors. The control signals originated either from a thermopile (Honeywell Radiamatic Head) heated by radiant heat transmitted from the susceptor by means of a sapphire light pipe, or from a rectified signal taken from a coil adjacent to one of the rf leads. The first maintains a constant temperature at a point in the susceptor and the second a constant input power level. Both were used successfully, but the temperature fluctuations at the outer surface of the susceptor, induced by convective heat losses, make the rf power sensor better suited to high-pressure (P > 300 psig) crystal growth. At fixed control points, the temperatures at the bottom of crucibles remained within $\pm$0.2°C at temperatures up to 1250°C and furnace pressures up to 30 psig when the light pipe-Radiamatic Head sensor was used and within $\pm$1.0°C at temperatures up to 1500°C and pressures of 800 psig with the rf power sensor.

Crystal growth runs were not made with the control signal originating from a thermocouple positioned either at the circumference of the central axis of the susceptor. Thermocouples positioned at the circumference did not prove reliable due to arcing to the grounded thermocouples from either the coil or the susceptor through the ceramic insulators. Thermocouples positioned at the central axis of the susceptor were not satisfactory for controlling the rf power level, since there is an excessive lag between a varied rf power level and the temperature response at this position.

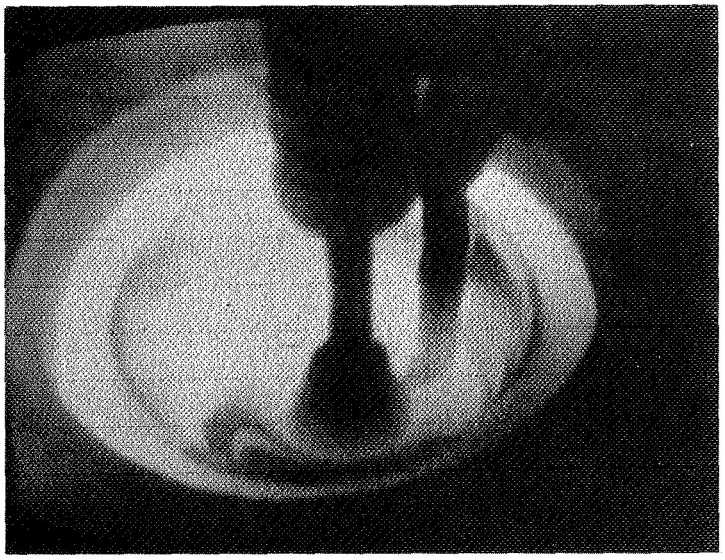

FIGURE 4. LIQUID ENCAPSULATED InP CRYSTAL GROWTH RUN VIEWED BY CLOSED CIRCUIT TELEVISION. BN SEED HOLDER, SEED, BOULE, SUSCEPTOR, CRUCIBLE AND RADIATION SHIELDS ARE DISTINGUISHABLE. AN ELECTRICAL CONTACT USED TO DETERMINE WHEN THE SEED AND MELT ARE JOINED IS SHOWN AT UPPER RIGHT HAND SIDE OF CRUCIBLE.

1. Czochralski Growth Station

The rf-heated Czochralski crystal growth station was designed to meet the following criteria:

(a) To achieve maximum uniformity of temperature in the susceptor.

(b) To have a large thermal mass, which reduced the rate of temperature fluctuations due to rf power level fluctuations.

(c) To reduce the axial temperature gradient in the crystals above the melt as far as possible while retaining coverage of the boules with the B_2O_3 encapsulant.

(d) To monitor temperature in a position that is closely related to the actual melt temperature.

The crystal growth station shown schematically in Figure 5 and in operation in Figure 6 achieved these goals for temperatures up to 1500°C and ambient gas pressures up to 800 psig. It proved rugged and reliable in operation while allowing maximum visibility of the growth process. The position of the growth station in the crystal growing furnace is shown in Figure 7. The dimensions of the susceptor and radiation shielding were varying slightly with different crucibles.

The graphite susceptor (Ultra Carbon Grade UF4S, Bay City, Michigan) was shaped and shielded to enhance uniformity of temperature in the vicinity of the crucible. The shielding consisted of two concentric fused-silica tubes and a pyrolytic graphite plate which supported the inner fused-silica tube. The inner tubular shield was translucent to increase the absorbtance of IR radiation from the susceptor; this reduced the temperature difference between this shield and the susceptor, which is a driving force for convective gas flow adjacent to the susceptor. It is essential that the shields fit their supports tightly to prevent the free flow of cooled gas into the bottom of the growth station. The outer convective shield is not necessary for growth at pressures below 30 psig. Gallium arsenide and gallium phosphide crystals were grown from 2-inch ID SiO_2 crucibles using a larger susceptor which closely fits the outer radiation-convection shield.

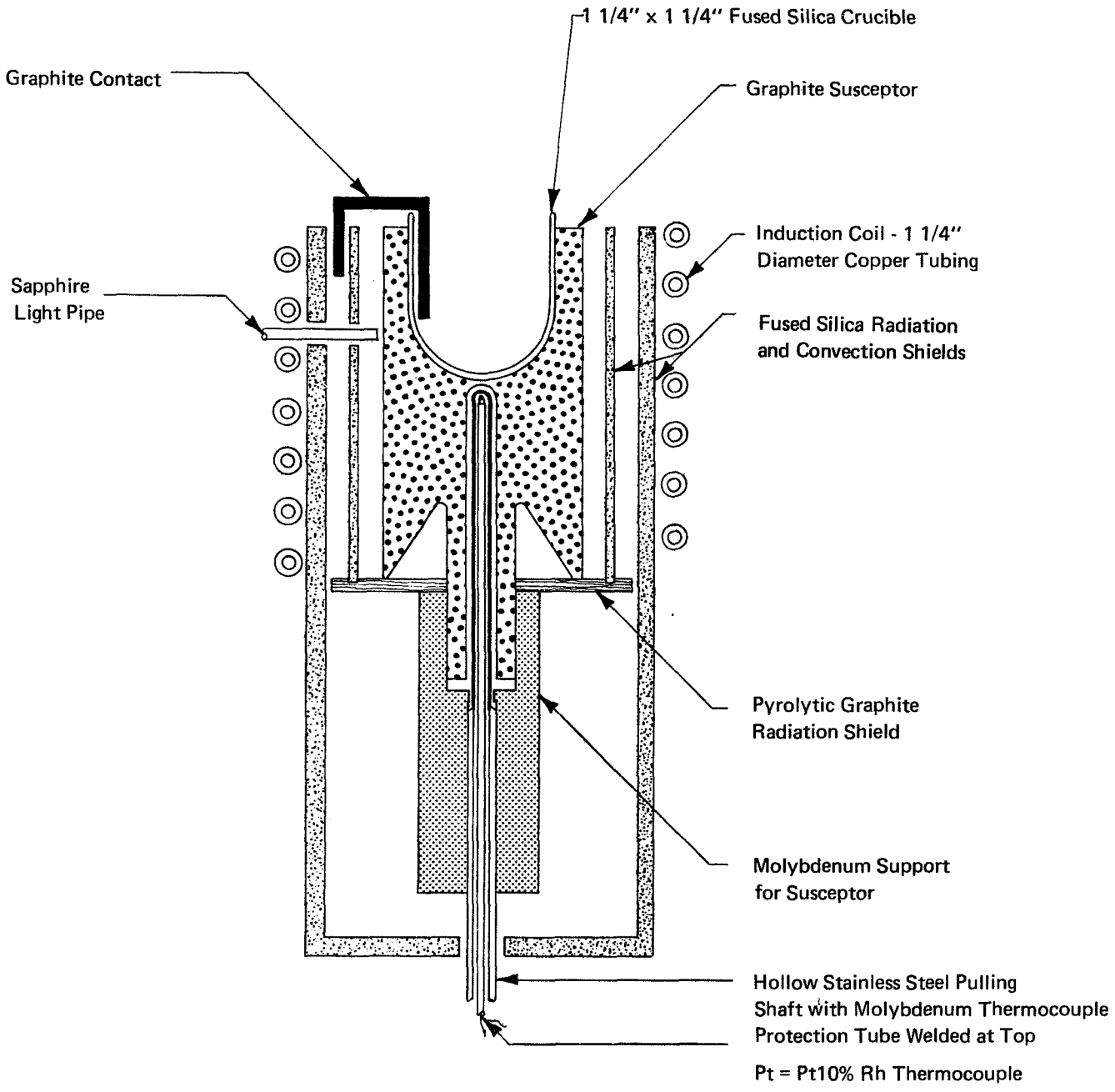

FIGURE 5 CRYSTAL GROWTH STATION USED FOR HIGH PRESSURE GROWTH RUNS (2/3 Scale)

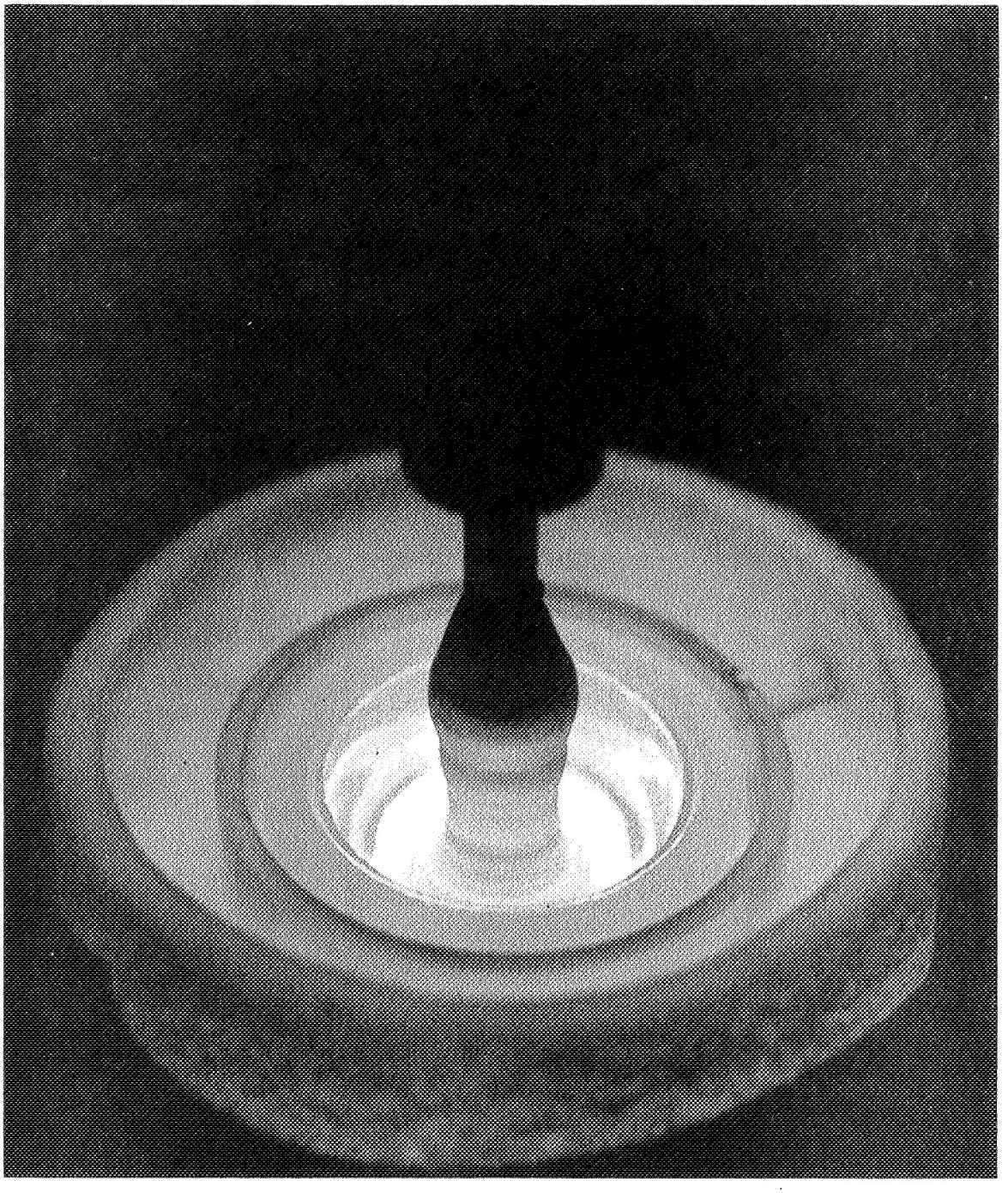

FIGURE 6 LIQUID ENCAPSULATED GaAs CRYSTAL GROWTH RUN

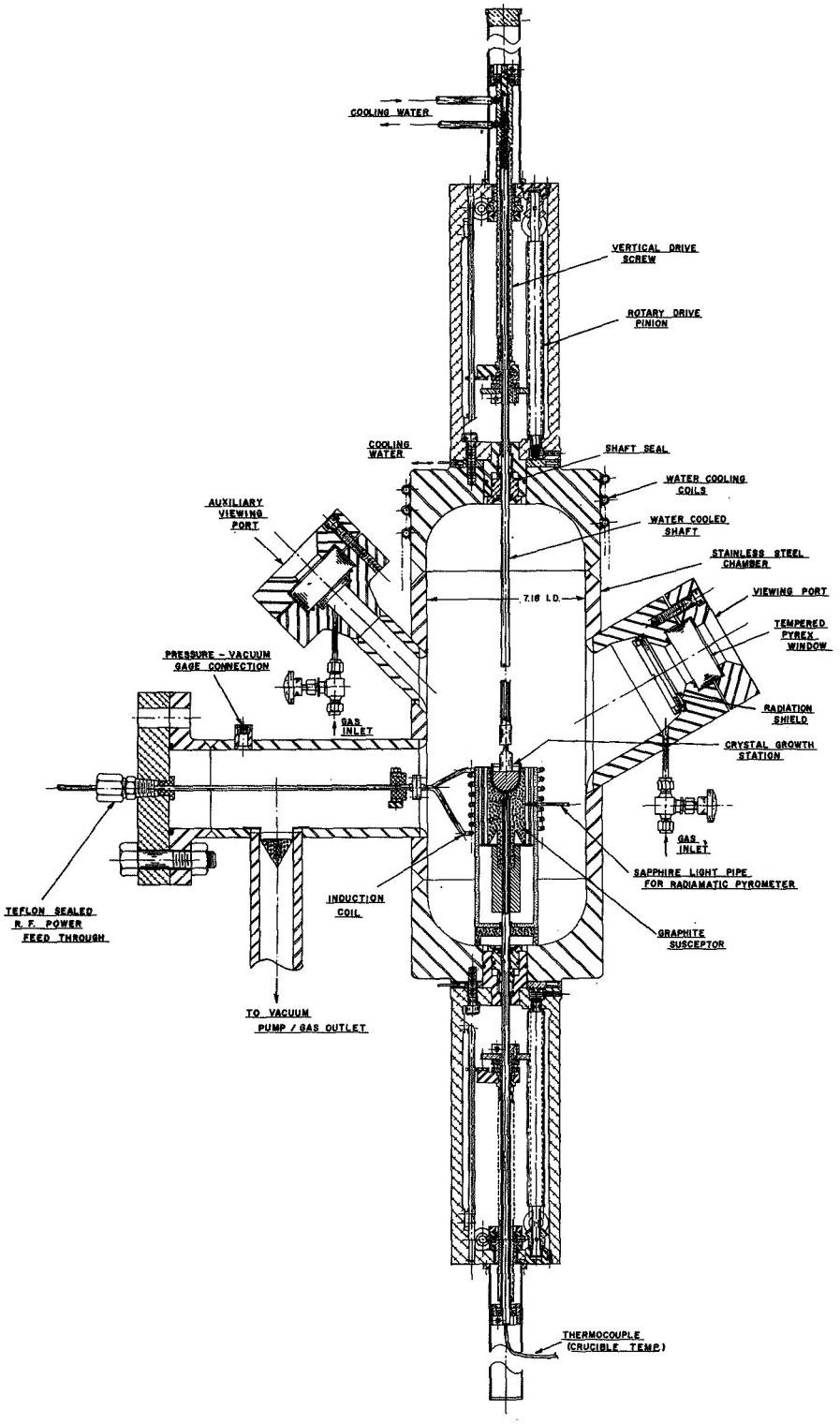

FIGURE 7 CROSS SECTION OF MODEL HP CRYSTAL GROWING FURNACE

The completion of an electrical circuit was used to indicate when a seed contacted the surface of a melt during remotely operated high-pressure crystal growth experiments. The seed was in electrical contact with the grounded upper pulling shaft. A high-purity graphite contact, shown in Figure 5, extended into the melt (contained in a fused-silica crucible) without touching the grounded susceptor. The graphite contact was grounded when the seed contacted the melt surface. A d-c ohmmeter was used to indicate when the circuit was completed. The B_2O_3 has a sufficiently high resistance that little current flowed when the seed was only in the B_2O_3, and a marked change in resistivity was evident when the surface of the melt was first contacted.

An a-c contacting circuit (Figure 8) was designed but never used, due to the termination of the program; its advantages over the d-c circuit include avoiding contamination by the probe and the use of conductive crucibles.

Growth temperatures were monitored by a thermocouple positioned at the bottom of the crucible along the central axis of the susceptor in Figure 5. Platinum vs. platinum-10% rhodium thermocouples proved reliable up to 1400°C when isolated from the graphite susceptor by a tantalum protection tube. Molybdenum protection tubes were used in earlier runs, but above 1400°C (needed for GaP) molybdenum recrystallizes and becomes embrittled; thus, they often failed due to stresses induced by the mismatch in thermal expansion coefficients between them and the stainless steel support shaft or by improper handling.

Tungsten 5% rhenium vs. tungsten 26% rhenium thermocouples were used up to 1600°C without a protection tube, but only in high-pressure, high-temperature growth runs, since they also become embrittled during use and are less reliable than the platinum thermocouples. Their junction voltage is relatively high compared with that of other thermocouples, but it is not as reproducible as that of the platinum-based thermocouple. Each batch of thermocouple wire used in these experiments was traceable to NBS standards.

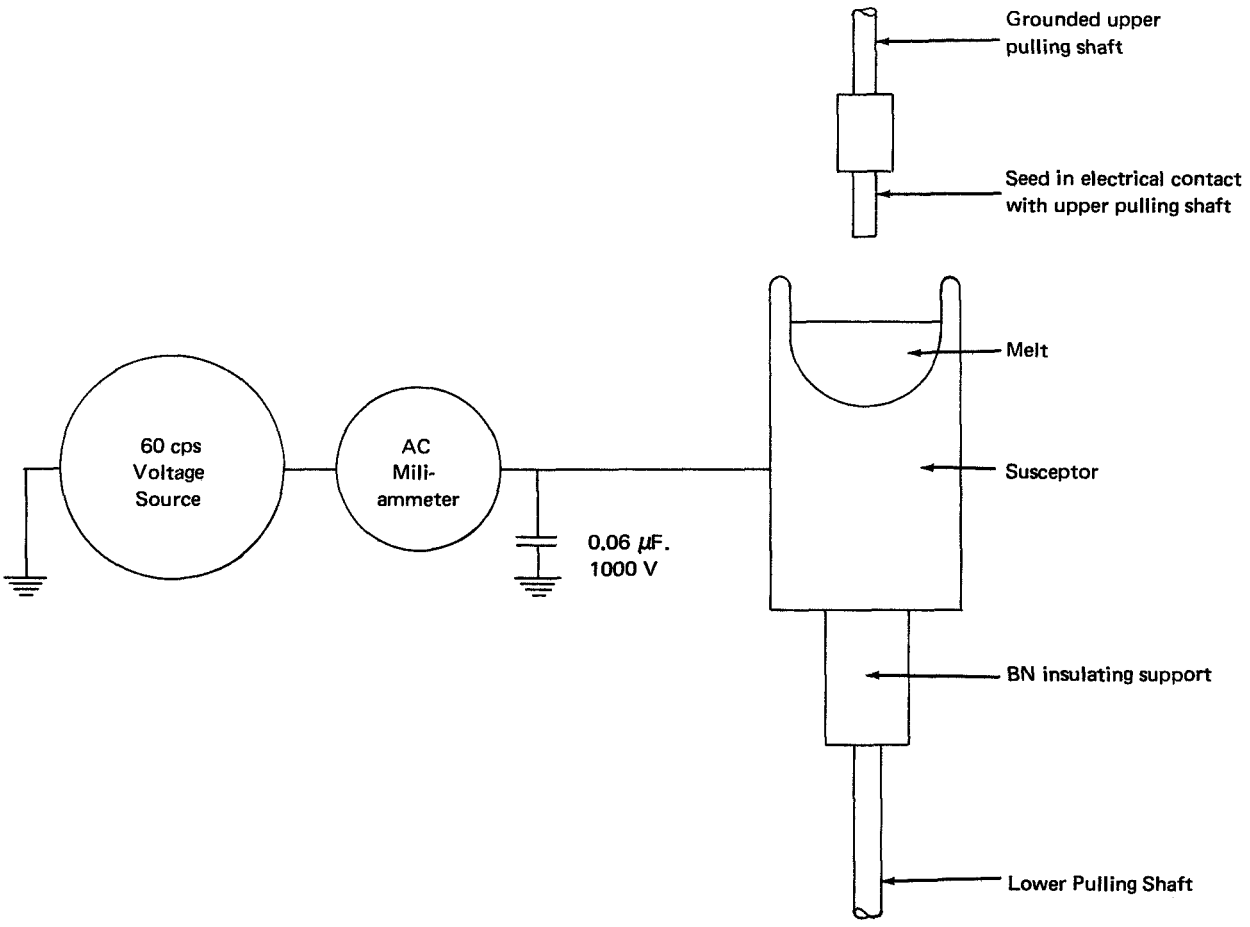

FIGURE 8 SCHEMATIC OF A.C. CIRCUIT TO INDICATE WHEN SEED IS IN CONTACT WITH MELT

2. Bridgman Growth Station

The Bridgman growth station, shown in Figure 9, was used in unidirectional solidification runs with non-stoichiometric InP. Heat was transferred from an rf-heated susceptor to a graphite crucible support. Metallographic analysis showed that the heat losses were parallel to the longitudinal axis of the crucible as intended. The vitreous silica convection shield fitted the graphite base snugly to prevent free flow of gas along the crucible. Temperature was measured by means of a thermocouple positioned adjacent to the tip of the crucible. A typical temperature history profile is shown in Figure 10.

3. Crucible Materials

The choice of crucible materials is greatly limited for liquid-encapsulated crystal growth, because the crucible must be inert to both the molten encapsulant and the contained melt. High-purity Al_2O_3, fused silica, vitreous carbon, and pyrolytic BN have been discussed in the literature as crucibles for III-V melts encapsulated by B_2O_3. On another program it was found that Al_2O_3 crucibles were dissolved rapidly by molten B_2O_3. Crucibles of both vitreous carbon (Vitreous Carbons, Ltd., Evenwood, England) and fused silica (Type 204 quartz, General Electric Co.) have been used successfully during the program. The B_2O_3 sticks to both materials sufficiently to break the crucibles upon cooling to room temperature. None of the compounded melts appear to wet or stick to either crucible material. Antimony, used to make up GaSb and InSb melts from mixed elements, appears to wet vitreous carbon.

Pyrolytic BN crucibles were used extensively in later runs with great success. Initial experiments with these crucibles for degassing the B_2O_3 encapsulant were discouraging, since BN chips were found in the degassed B_2O_3. This did not prove to be a problem in the crystal growth runs, however; the spalling apparently occurs only on cooling. All of the III-V charges were easily removable from Czochralski and Bridgman crucibles after the B_2O_3 encapsulant was dissolved in warm water. The stresses in the crucibles resulting from the high thermal expansion coefficient of the adherent B_2O_3 were relieved by

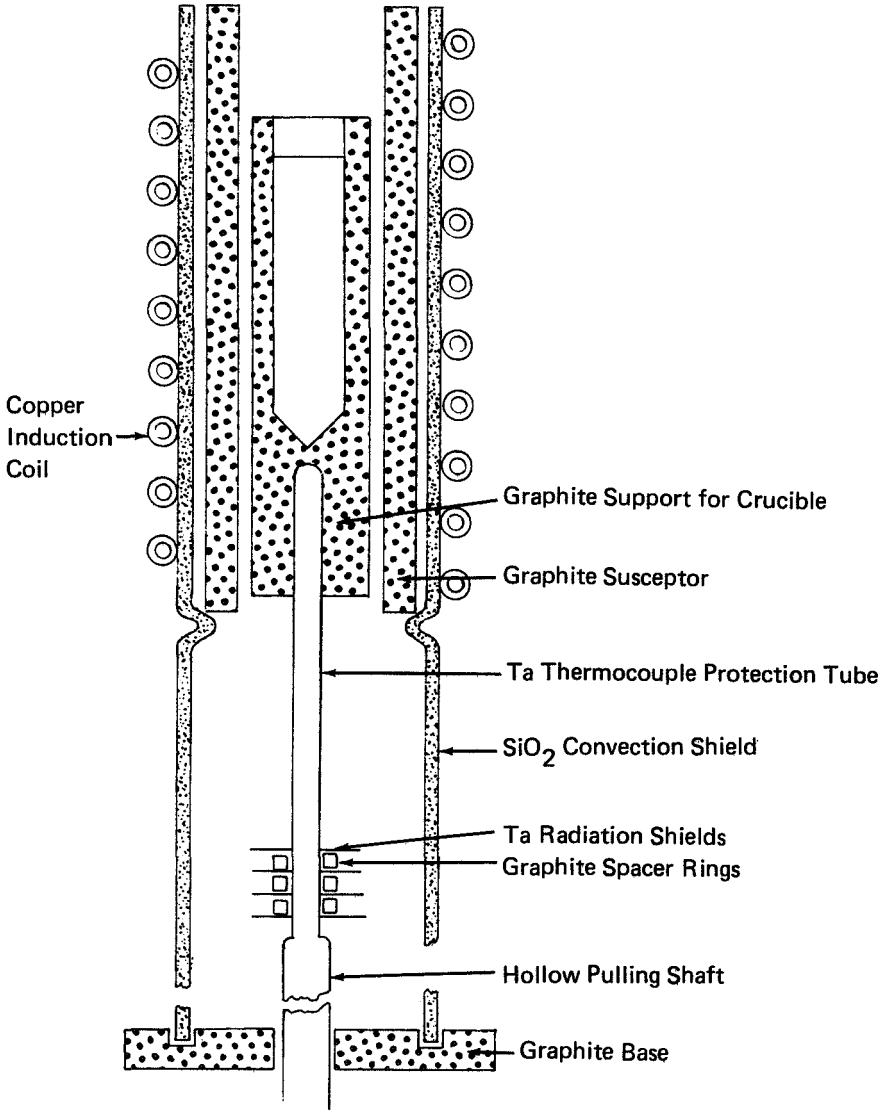

FIGURE 9 BRIDGMAN GROWTH STATION
(2/3 Scale)

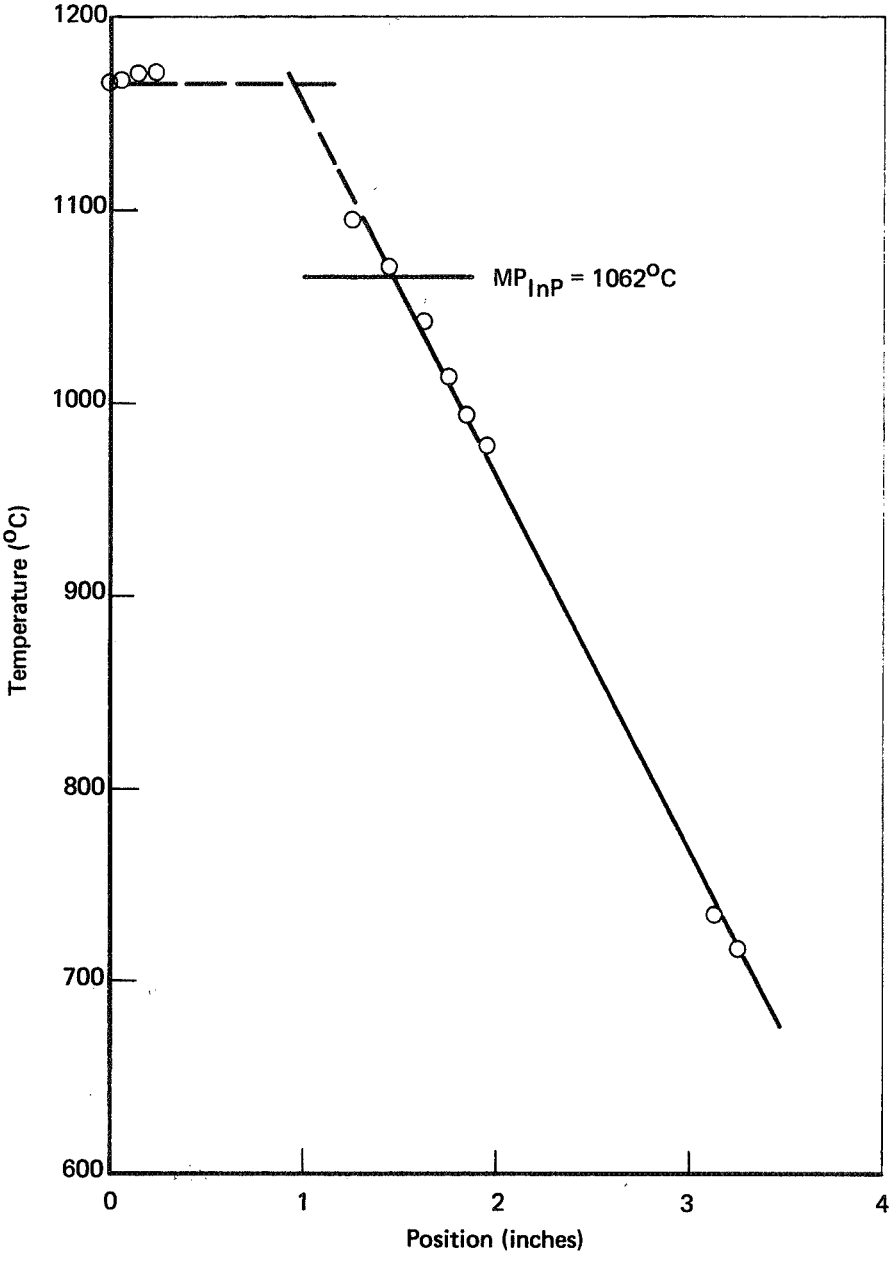

FIGURE 10 TYPICAL TEMPERATURE HISTORY FOR InP BRIDGMAN SOLIDIFICATION RUNS

delaminating the pyrolytic material rather than breaking the crucibles as was the case with vitreous carbon and fused silica crucibles. Since crucibles could be used as many as 15 times, their effective cost per run was comparable to that of the less expensive crucibles.

B. LIQUID ENCAPSULANT

The highest purity B_2O_3 commercially available in lump form was produced by the British Drug House, Pool, Dorset, England during the experimental portion of the program. Material purchased from this source was used exclusively during the program. (Even though the B_2O_3 may be quite free of metallic impurities, it contains relatively large quantities of dissolved water when received from the manufacturer. It hydrates so quickly when exposed to the atmosphere that it is impractical to attempt shipment of material which is free of absorbed and dissolved water. This water must be removed from the B_2O_3 prior to its usage as an encapsulant for these high-purity III-V melts to prevent oxygen contamination.)

The water was removed by vacuum-melting small quantities of the glass. The furnace used for this purpose, shown in Figure 11, has a resistance-heated graphite element surrounding the crucible. Mechanical and oil diffusion pumps were used to achieve a vacuum of 10^{-4} torr at temperature. Fifteen- to twenty-gram charges of B_2O_3 were vacuum-melted to 1200°C at a pressure of 10^{-3} torr prior to useage in crystal growth experiments. (See Appendix B for handling procedures.) The charges were cooled to room temperature prior to removal from the vacuum furnace, because the rate of rehydration increased visibly if the B_2O_3 was only slightly warm when exposed to a humid atmosphere. The degassed B_2O_3 charges were stored in a desiccator evacuated to 25 microns Hg. Charges have been stored for as long as three weeks with no visible evidence of contamination by water.

Several crucible materials were investigated for degassing the B_2O_3. Platinum has been used[(2)], but it was found that the B_2O_3 stuck tenaciously to the crucibles. Removal of the degassed B_2O_3 from platinum

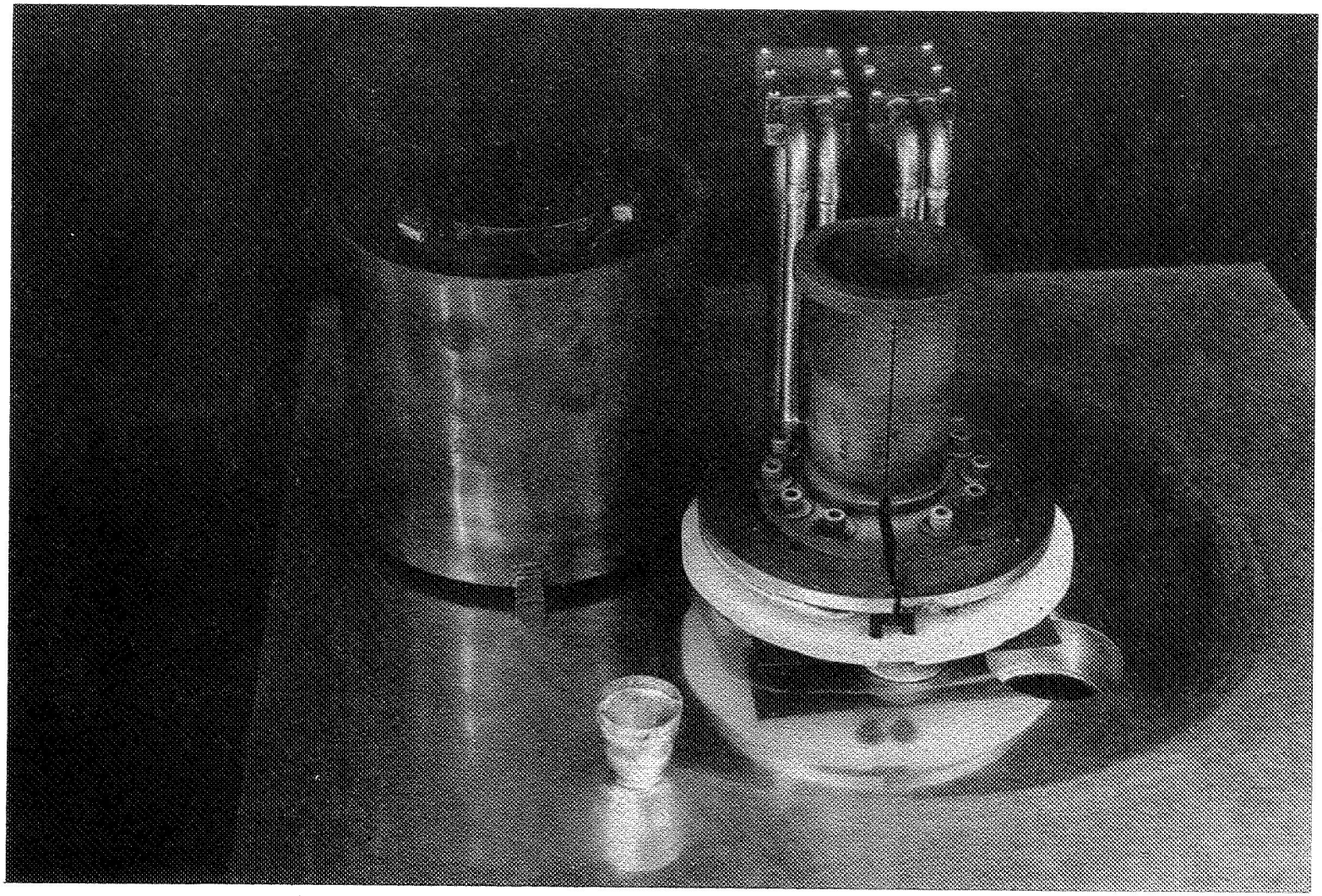

FIGURE 11 RESISTANCE HEATER ELEMENT, HEAT SHIELDS AND CRUCIBLE FOR THE VACUUM FURNACE USED TO DEGAS B_2O_3

crucibles resulted in both degrading the crucibles and fracturing the charge, which exposed a large surface area to rehydration. B_2O_3 stuck to and broke vitreous carbon and fused-silica crucibles. Chips of BN were observed in the glass after degassing in pyrolytic BN crucibles. They also had to be broken from the degassed glass, which was prohibitively expensive. Removal of the crucible chips from the dehydrated B_2O_3 did not appear a reasonable approach.

It was found that B_2O_3 does not stick to crucibles made from either 95% Pt-5% Au or 30% Pt-70% Au alloys (Engelhard, Inc., Carteret, New Jersey), and the degassed charges can be removed intact. Initially, the B_2O_3 comes free of the 30% Pt-70% Au crucibles more easily than those made of the 95% Pt-5% Au alloy, but after several 1200°C runs in vacuum, the former become thermally etched at grain boundaries and the B_2O_3 charge is "locked" in by mechanical interference. A single 95% Pt-5% Au crucible has been used to degas most of the B_2O_3 used during this program with little sign of wear.

Another approach for handling the degassed B_2O_3 is to cast shaped discs by pouring it into cold molds while in vacuum.

C. MELT-DOWN OF ENCAPSULANT AND CHARGE

A two-step melting sequence was found desirable for minimizing the loss of volatile components from B_2O_3-encapsulated melts. The B_2O_3 was melted at approximately 650°C in vacuum ($P \leq 10^{-3}$ torr). Vacuum melting served two essential functions: any water absorbed during handling was removed from the B_2O_3, and the molten B_2O_3 could freely percolate down through the charge and completely fill all voids. If these voids were filled with gas rather than B_2O_3, large numbers of bubbles would rise through the B_2O_3 encapsulant when the charge was melted, allowing the loss of volatile component (As or P) from the melt.

After the B_2O_3 was thoroughly degassed (i.e., when the pressure returned to approximately 10^{-5} torr), the ambient gas was introduced into the furnace. With rf heating it is important that the power be turned off prior to closing the valve to the vacuum system, or arcing

and/or the formation of a corona is likely. This must be avoided, since it would likely introduce copper as an impurity to the melt.

Once the furnace atmosphere was established and the power was turned on again, the temperature was quickly raised to the operating level. After the charge had melted, crystal growth followed conventional Czochralski procedures.

D. SYNTHESIS OF COMPOUNDS

InSb, GaSb, GaAs, and GaP intermetallic compounds were synthesized directly from condensed-phase component elements. High-quality single crystals were grown from all of these synthesized melts except GaP. The techniques required for the arsenide and phosphide differed from those used for the antimonides because of the high arsenic and phosphorus vapor pressures.

Stoichiometric quantities of gallium or indium were mixed with antimony. Synthesis was accomplished by heating the mixtures to temperatures in excess of the compounds' melting points, soaking for one hour, freezing, remelting, and cooling to room temperature. No problems with uncontrolled heating were encountered in the exothermic reaction with approximately 100-120 gm mixtures of component elements. Crystals were not grown from these melts immediately after reaction, but there is no practical reason why this could not have been done.

In both cases, a solid film formed on the surfaces of the antimonide melts immediately after reaction. The impurity responsible for the film, presumably oxygen, is believed to have originated in the elements (Ga 99.9999% United Mineral & Chemical Co., In 99.999% origin unknown, Sb 99.999% Cominco American Inc.), since it could be eliminated by subsequent processing of the reacted charges. The details of the techniques employed to remove the film are given in the discussions of the specific materials.

Three GaAs synthesis runs (approximately 140 gm/run) were successfully completed using a molten B_2O_3 encapsulant and ambient gas pressures up to 800 psig to suppress arsenic losses. Arsenic losses in three prior

runs, which were made in the standard MP crystal growing furnace, could not be controlled due to insufficient pressure capability. This possibility was anticipated, but the use of the high-pressure HP furnace for these synthesis experiments was postponed to avoid As contamination in the furnace chamber.

The arsenic and phosphorus partial pressures in equilibrium with elemental arsenic and phosphorus are shown in Figure 12 as a function of temperature. The As partial pressure at the melting point of elemental As ($\simeq$ 20 atm @ 814°) coincides with the maximum pressure limit of the standard MP crystal growing furnace. The first synthesis experiments were carried out to determine if the reaction

$$Ga\ (\ell) + As(s) \rightarrow GaAs(s)$$

would proceed to completion and, if the reaction

$$Ga\ (\ell) + As(\ell) \rightarrow GaAs(s)$$

proceeded, whether the exothermic reaction rate could be controlled to keep the As partial pressure from exceeding the 300-psi limit of the standard MP furnace.

None of these experiments proved successful. The reaction between liquid Ga and solid As does not proceed, even when the elements are made up of intimately-mixed, fine powders. Then the As melted, partial reaction between the elements occurred rapidly, and a large fraction of the As (and B_2O_3) was lost from the melt with an ambient gas pressure of 300 psi.

In the three runs made in the high-pressure HP furnace, the arsenic vapor was successfully contained with ambient pressure of 800 psi. A flash of light from the charge and a sudden rise in the indicated temperature were observed at a thermocouple reading of approximately 710-760°C. The top of the susceptor was visibly hotter than the region adjacent to the position of the thermocouple, so it is likely that the rapid reaction coincided with the melting of the As.

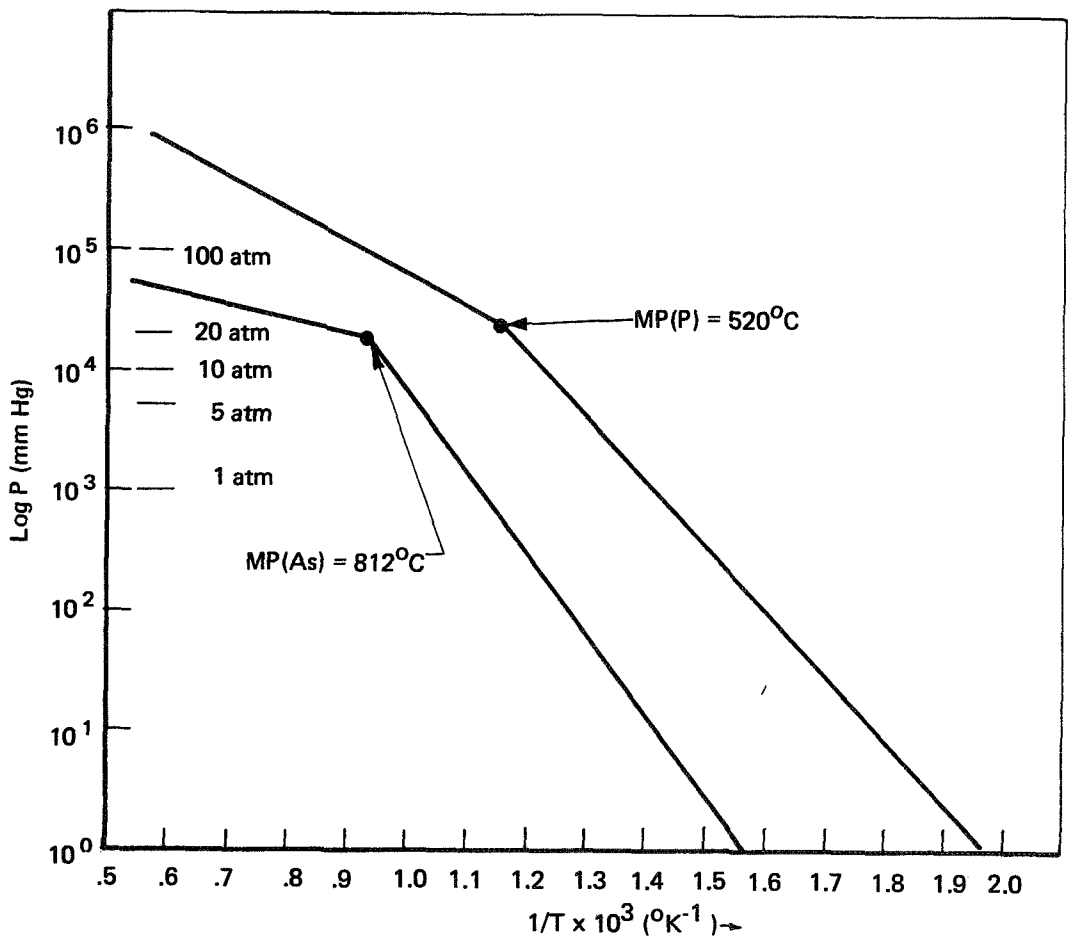

FIGURE 12 ARSENIC AND PHOSPHOROUS (RED) VAPOR PRESSURES IN EQUILIBRIUM WITH THE ELEMENTS

The following heating cycle was used in the sixth GaAs synthesis run and was found entirely satisfactory:

(a) $T \simeq 300°C$
$P = 10^{-4}$ torr
12 hours

Degas susceptor
Vaporize arsenic oxide

(b) $T \rightarrow 425°C$
$P \rightarrow 25$ psi
2-4 hours

Flow B_2O_3
over charge

(c) $T \rightarrow 525°C$
$P \rightarrow 800$ psig
1-2 hours

Drive B_2O_3
into voids in charge

(d) $T \rightarrow 1450°C$
$P = 800$ psi
1 hour

React elements and
form GaAs melt

(e) $T = 1450$
$P = 800$ psi
1 hour

Homogenize
melt

(f) $1450 \rightarrow 1200 \rightarrow 1450°C$
$P = 800$ psi
1/2 hour

Freeze and remelt to
homogenize melt

(g) $T \rightarrow$ room temp
$P \rightarrow 20$ psi
1/2 hour

During steps (a) and (b) the susceptor is positioned low in the rf coil to induce an inverted, steep axial temperature gradient and allow the B_2O_3 to flow without heating the unreacted As excessively. Once the B_2O_3 is forced into the voids in the charge, after step (c), the susceptor is raised in the rf coil until a uniform temperature is induced in the susceptor. It is retained in this position throughout the remainder of the synthesis run.

Two attempts were made to form GaP from stoichiometric mixtures of gallium and red phosphorus generally following the procedures used for GaAs but with ambient furnace pressures of 1250 psig of argon. All of the phosphorus was lost from the charge during the first synthesis run. Approximately 35% of the phosphorus reacted to form GaP in the second synthesis run.

A systematic series of GaP synthesis experiments could not be pursued because of funding and time limitations imposed by the program;

however, two experiments were undertaken with ADL funding because of the intense interest in the material. At this time, there is no clear explanation for the phosphorus losses. The B_2O_3 flowed over the charge before any phosphorus was visibly lost. Losses were evident as soon as the susceptor became visibly red (thermocouple temperature at bottom of crucible was approximately 350°C); however, no rapid exothermic reaction was observed as was the case with GaAs. The phosphorus was probably not entirely reacted at the time that the temperature corresponding to a phosphorus vapor pressure of 1250 psig (approximately 780°C) was reached. Phosphorus was then probably lost either in the form of vapor bubbles floating up through the B_2O_3 encapsulant or perhaps the bubbles may have become attached to phosphorus particles and carried them up through the B_2O_3. There is also some uncertainty as to whether red phosphorus has a higher density than B_2O_3 over the entire temperature range, because data are limited and conflicting. The results of these two experiments were encouraging, but further work is required to optimize process parameters.

Crystal growth runs were not undertaken directly after GaAs synthesis, although they clearly could have been. The B_2O_3 encapsulant was clear, and the surface of the reacted melt was clean. This synthesis technique offers economic and probable technical advantages over conventional vapor-phase synthesis. Large quantities of compound material can be synthesized rapidly (in fact, all steps of the reaction procedure can be done more rapidly) from inexpensive component elements, and Czochralski crystal growth can be initiated without further handling. Dopants can be added prior to synthesis.

E. CHARACTERIZATION OF MATERIALS

Incoming materials and crystals grown during the program were characterized chemically by emission- and spark-source mass spectrographic analyses and electrically by Hall measurements. X-ray topography and dislocation etch pit techniques were used to lesser extents to characterize the crystallographic quality of the crystals. X-ray fluorescence analyses were used in a few cases for preliminary analyses.

Emission spectrographic analyses were made principally by the Jarrel-Ash Division of Fisher Scientific Co., Waltham, Massachusetts, and Monsanto Co., St. Peters, Missouri. Spark-source mass spectrographic analyses were carried out by Bell & Howell, Pasadena, California. Samples submitted for chemical analysis were chemically polished (Appendix C-2) and thoroughly rinsed prior to shipment in sealed polyethylene bags. Both Bell & Howell and Monsanto re-etched the samples before making their analyses.

IV. CRYSTAL GROWTH EXPERIMENTS AND RESULTS OF CRYSTAL CHARACTERIZATION

A total of 55 crystal growth experiments (plus 13 synthesis experiments) were made during this contract with undoped GaAs, InAs, GaP, InP, GaSb and InSb. The growth parameters, furnace atmospheres, brief observations, and results of chemical and electrical characterization are given in Tables 2 through 14. The results of the spectrographic analyses of two lots of B_2O_3, before and after degassing, are given in Table 1.

In Tables 1, 3, 5, etc., which present the results of spectrographic analyses carried out at the Jarrel-Ash Co., the symbols represent the following:

VVFT	$\leq$	0.0001% (by weight)
VFT		0.0001 - 0.001%
FT		0.001 - 0.01%
T		0.01 - 0.1%
L		0.1 - 1.0%
M		1.0 - 10.0%
H	$\geq$	10.0%

The Hall measurements made at ADL and at Monsanto Co. were all carried out at room temperature with the exception of those made on InSb. The latter were made in a liquid N_2 bath at -195°C. Hall characterization of some high-resistivity GaAs and GaP samples were made at NASA/ERC.

Photographs of representative III-V boules grown during this contract are shown in Figures 13 through 17.

TABLE I

CHEMICAL ANALYSES OF B_2O_3 SAMPLES AND VITREOUS CARBON CRUCIBLE

(percent by weight*)

	Lot #1		Lot #2		Vitreous Carbon			
Element	As Received	Degassed	As Received	Degassed				
B	H	H	H	H				
Mg	VFT FT	VFT FT	VVFT	VVFT		VVFT VFT		
Al	VVFT	VVFT	VVFT	VVFT		VVFT -VFT		
Si	VFT	FT		VFT		VFT		
Ca	VFT					VVFT		
Cr						VVFT -VFT		
Mn	VVFT	VVFT						
Fe	VFT					VVFT -VFT		
Cu	VVFT	VVFT				VVFT -VFT		
Ag	VVFT	VVFT						
Sn		FT				VVFT -VFT		
Pb						VVFT		
		*See text for explanation of symbols.						

TABLE II

SUMMARY OF GaAs CRYSTAL GROWTH EXPERIMENTS

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr.)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
1	<111>	3/4	18	0.45	A	70	Vitreous Carbon		Boule became polycrystalline after 1" of growth. Boule partially remelted.
2	<111>	3/4	18	0.45	A	75	Vitreous Carbon	38.5	No wetting by B_2O_3. One growth twin.
3	<111>	1/2	18	0.6	H_2/A	75	Vitreous Carbon	42.6	Boule was polycrystalline by end of run. Seed direction did not carry through neck. Film was noticed on GaAs melt. No wetting by B_2O_3. Several growth twins.
4	<111>	3/4	18	0.75	H_2/A	15	Vitreous Carbon	22.91	Melt surface remained clean throughout run. No wetting by B_2O_3. Several growth twins.
5	<111>	3/4	18 & 8	0.75	H_2/A & N_2	15→4	Vitreous Carbon		Increased power level required to maintain melt when N_2 substituted for H_2/A gas. Film on surface of melt began to nucleate bubbles at 8 psig. Melt cleared at pressure of 4 psig N_2. Boule polycrystalline from neck. No wetting by B_2O_3. Boule remelted.
6	Demonstration run - scrap material								
7	<111>	1/2	8	0.6	N_2	9.5→3	2 x 2 SiO_2	34	Substantially reduced As loss and thermal etching. Melt held just prior to meltdown until bubbles stopped coming off GaAs charge. One growth twin eliminated by necking down. Melt clean throughout run. Good single crystal. Arced during meltdown.
8	<111>	1/2→3/4	8→18	0.6	N_2	9	Vitreous Carbon	45	Surface of melt covered with film which was displaced during seeding by freezing surface & remelting. Surface tended to freeze from one side which limited diam. of crystal. Vitreous carbon crucible not baked out prior to use.

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TABLE II (Continued)

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr/)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
9	<111>	3/4	8	0.6	N_2	9	2 x 2 SiO_2	33	Attempt to grow large (4cm diam) crystal. Surface of melt tended to solidify during growth cond.
10	<111>	3/4→1/4	8	0.6	N_2	6	2 x 2 SiO_2	120	Attempt to grow 4 cm diam. Susceptor lowered in coil from position used for runs 8 and 9. Surface okay. Got 3.4 cm diam. boule which was single.
11	<111>	3/4	8	0.75	N_2	20	1-1/4 x 1-1/4 SiO_2	36	First run with B & H material. Arced during growth in He atm. Changed to N_2. Boule polycrystalline.
12	<111>	---	---	1.15	N_2	6	1-1/4 x 1-1/4 SiO_2		Ta wire holding seed oxidized and seed dropped into melt.
13	<111>	1/2	8	0.87	N_2	8	1-1/4 x 1-1/4 SiO_2	35.8	No coverage of boule by B_2O_3. Molten Ga on boule ran down to solidification interface and resulted in twinning.
14	<111>	3/4	8	1.24	N_2	4	1-1/4 x 1-1/4 SiO_2		Run terminated because B_2O_3 not covering boule. Boule had trapped Ga aligned along the growth axis and was not single crystal.
15	<111>	0.95	8	0.88	N_2	15	1-1/4 x 1-1/4 SiO_2	34.4	Boule not covered by B_2O_3. Free Ga apparent on surface of boule. Frequent twinning.
16	<111>	1.0	10	0.85	N_2	15	1-1/4 x 1-1/4 SiO_2	19.3	Run made with nondegassed B_2O_3 and susceptor top level with upper coil. No coverage of boule. Susceptor raised 1/4" above coil and greatly reduced thermal etching of boule without covering single crystal boule.

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TABLE II (Continued)

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr.)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt(gm)	Comments
17	111	1-1 1/2	8	1.0	N_2	15	Vitreous Carbon	46.5	Nondegassed B_2O_3 used in run with susceptor approximately 1/4" above coil. No coverage of boule but no evidence of thermal etching. Controller failed during run and boule twinned during rapid temperature changes.
18	<111>	3/4	8	1.7	N_2	15	Vitreous Carbon	32.5	B_2O_3 very clean. Got partial coverage of single crystal boule with essentially no thermal etching.
19	<111>	1/2	8	0.8	N_2	20	1-1/4x1-1/4 SiO_2	40.2	B_2O_3 very clean. Got partial coverage of single crystal boule with essentially no thermal etching.
20	<111>	1/2	8	0.8	N_2	20	Vitreous Carbon	40.7	B_2O_3 very clean. Got no thermal etching of boule. Two growth twins.
21	<111>	1/2	8	0.8	N_2	15	BN	38.2	B_2O_3 very clean. No coverage of single crystal boule but little thermal etching.
22	<111>	1/2	8	0.8	N_2	16	BN	60	B_2O_3 very clean. No coverage of single crystal boule but little thermal etching.
23	<111>	1/4	8	0.95	N_2	20	3 x 2 SiO_2	~200	Seed holder broke after boule expanded to over 2-inch diameter. Boule polycrystalline. No coverage of boule with B_2O_3.
24	<111>	1/8	8	0.95	N_2	15	3 x 2 SiO_2	~300	Boule diameter exceeded 2-1/2 inches. Boule twinned. No coverage of boule with B_2O_3.

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TABLE III

CHEMICAL AND HALL ANALYSES OF GaAs SAMPLES

(percent by weight)

	Raw Material		GaAs-2		GaAs-3		GaAs-4	
Element	G-273 (O2doped)	G4-58 (regular)	Top	Bottom	Top	Bottom	Top	Bottom
B				VVFT	FT-T	VVFT	VVFT	VVFT
Mg	VVFT	VVFT		VVFT	VVFT VFT	VVFT	VFT	VVFT
Al	VVFT	VVFT		VVFT	VFT	VFT	VFT	VVFT
Si	VVFT	VVFT VFT		VFT	VFT	VVFT	FT	VFT
Ca	VVFT	VVFT		VVFT	VVFT	VVFT	VFT	VVFT VFT
Mn							VVFT	
Fe					VVFT	VVFT	VVFT VFT	VVFT VFT
Cu	VVFT	VVFT VFT		VVFT	VVFT VFT	VVFT	VFT	VVFT
Ga	H	H		H	H	H	H	H
As	H	H		H	H	H	H	H
Ag	VVFT						VVFT	
Sn							VVFT	VVFT VFT
Pb							VVFT	
	Raw Material							
Origin	Monsanto	Monsanto	Monsanto		Monsanto		Monsanto	
Carrier Conc	$0.8\text{-}1.2\times10^{15}$	$2.4\text{-}3.1\times10^{15}$	$1.2\text{-}2.1\times10^{16}$		$1.2\text{-}2.1\times10^{16}$		$1.2\text{-}2.1\times10^{16}$	
Mobility	4700	5400	4300-7100		4300-7100		4300-7100	
Type	n	n	n		n		n	
	Boule							
Carrier Conc			1.22×10^{16}	4.3×10^{16}		9.7×10^{15}		1.2×10^{16}
Mobility			42	24.3		100		640
Type			p	p		p		p
Crucible			Vitreous Carbon		Vitreous Carbon		Vitreous Carbon	

TABLE III (Continued)

	GaAs-7		GaAs-8		GaAs-9		GaAs-11	
Element	top	bottom	top	bottom	top	bottom	top	bottom
B			VVFT VFT	VVFT VFT		VVFT		VVFT
Mg		VVFT	VVFT VFT	VVFT		VVFT	VVFT VFT	VVFT
Al		VVFT VFT	VFT	VVFT VFT		VVFT		VVFT VFT
Si		VVFT	VFT	VVFT VFT		VVFT	VVFT	VVFT
Ca			VVFT VFT	VVFT		VVFT		
Mn								
Fe		VVFT	VVFT VFT	VVFT VFT		VVFT	VVFT	
Cu		VVFT	VVFT VFT	VVFT VFT		VVFT		
Ga		H	H	H		H	H	H
As		H	H	H		H	H	H
Ag								
Sn			VVFT	VVFT		VVFT		VVFT
Pb							VVFT	
	Raw Material							
Origin	Monsanto		Monsanto		scrap		Bell & Howell	
Carrier Conc	2.7×10^{15}		$0.8\text{-}1.2 \times 10^{15}$				1×10^{16}	
Mobility	5400		4700				4960	
Type	n		n				n	
	Boule							
Carrier Conc		1.3×10^{16}	5.5×10^{15}	3.3×10^{16}		4.8×10^{18}	4.5×10^{15}	
Mobility		32	310	230		1430	5.7×10^{3}	
Type		p	p	p		n	n	
Crucible	SiO_2		Vitreous Carbon		SiO_2		SiO_2	

TABLE III (Continued)

	GaAs-13		GaAs-16		GaAs-17		GaAs-18	
Element	top	bottom	top	bottom	top	bottom	top	bottom
B				VVFT		VVFT		VVFT
Mg	VVFT			VVFT				
Al	VVFT	VVFT		VVFT		VVFT		VVFT
Si	VFT	VFT		VVFT		VVFT		
Ca								
Mn								
Fe				VVFT				VVFT
Cu	VVFT			VVFT				
Ga	H	H		H		H		H
As	H	H		H		H		H
Ag								
Sn								
Pb								
	Raw Material							
Origin	Bell & Howell		Scrap		Scrap		Bell & Howell	
Carrier Conc	$3x10^{15}$							
Mobility	3000							
Type	n							
	Boule		$\rho = 8x10^{3}$ Ωcm	$\rho = 1.34x10^{5}$ Ωcm				
Carrier Conc	$3.6x10^{16}$	$2.4x10^{17}$				$2.3x10^{16}$		$2x10^{16}$
Mobility	$2.4x10^{3}$	$2.1x10^{3}$				58		290
Type	n	n				n		p
Crucible	SiO_2		SiO_2		SiO_2		Vitreous Carbon	

TABLE III (Continued)

	GaAs-19		GaAs-20		GaAs-21		GaAs-22	
Element	top	bottom	top	bottom	top	bottom	top	bottom
B	VVFT	VVFT	VVFT		VFT	VFT	FT	T
Mg	VVFT					VVFT	VVFT	VVFT
Al			VVFT		VVFT	VFT	VVFT -VFT	VVFT -VFT
Si	VVFT -VFT	VVFT			VVFT	VVFT -VFT	VVFT	VVFT -VFT
Ca								
Cr	VVFT -VFT	VVFT -VFT	VVFT		VVFT	VVFT		
Mn								
Fe	VVFT	VVFT			VVFT	VVFT		VVFT
Ni	VVFT -VFT	VVFT -VFT	VVFT					
Cu								
Ga	H	H	H		H	H	H	H
As	H	H	H		H	H	H	H
	Raw Material							
Origin	Bell & Howell		ADL		Bell & Howell		ADL	
Carrier Conc	1×10^{16}				9.5×10^{15}			
Mobility	4500				5200			
Type	n				n			
	Boule							
Carrier Conc	1.83×10^{7}	2.68×10^{15}	1.21×10^{17}		$2.5\text{-}5.8 \times 10^{13}$	3.8×10^{14}	1.43×10^{16}	8.93×10^{16}
Mobility	2250	285	2660		340-850	168	373	285
Type	n	p	n		n	p	p	p
Crucible	SiO_2		Vitreous Carbon		BN		BN	

TABLE III (Continued)

	GaAs-23		GaAs-24					
Element	top	bottom	top	bottom				
B								
Mg								
Al								
Si								
Ca								
Mn								
Fe								
Cu								
Ga								
As								
Ag								
Sn								
Pb								
	Raw Material							
Origin								
Carrier Conc								
Mobility								
Type								
	Boule							
Carrier Conc								
Mobility								
Type								
Crucible								

TABLE IV

SUMMARY OF InAs CRYSTAL GROWTH EXPERIMENTS

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr.)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
1	<111>	1/2	8	0.95	H_2/A	15→22	Vitreous Carbon		Boule polycrystalline. Pulling head not working properly. Arcing during run due to improper positioning of coil.
2	<111>	1/2	8	0.95	H_2/A	15	2 x 2 SiO_2		First boule polycrystalline. Pulling head not pulling smoothly. 2nd boule pulled by JFW good single crystal. Seed soaked ∿ 15 min prior to pulling. No wetting by B_2O_3.
3	<111>	1/2	3	0.60	H_2/A	12.5→2	2 x 2 SiO_2		Surface of melt covered with film when first melted. Got bubble nucleation on film particles when pressure reduced to 2 psig. Growth twins propagated length of boule rather than growing out.
4	<111>	1/2	8	0.60	N_2	15→3	2 x 2 SiO_2		Surface of melt covered with film. Melt soaked 22 hrs. in attempt to clean up. Did not even at 3 psig. Film displaced by freezing surface prior to pulling. Melt remained clean during initial phases of growth & again at end of run. Substantially reduced thermal etching of boule. No growth twins.

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TABLE V

CHEMICAL AND HALL ANALYSES OF InAs SAMPLES

(percent by weight)

	Raw Material		InAs-2		InAs-3		InAs-4	
Element	GI-23		Top	Bottom	Top	Bottom	Top	Bottom
B				VFT				
Mg	VVFT			VVFT VFT		VVFT	VVFT	VVFT
Al	VVFT VFT			VFT		VVFT	VVFT	
Si	VVFT VFT			VFT FT		VVFT	VVFT	VVFT
Ca	VVFT			VFT		VVFT	VVFT	VVFT
Mn				VVFT				
Fe	VVFT			VVFT VFT		VVFT	VVFT	
Cu	VVFT			VFT			VVFT VFT	VVFT
Ga	VVFT VFT							
As	H			H		H	H	H
In	H			H		H	H	H
Pb				VVFT		VVFT		
	Raw Material							
Origin	Monsanto		Monsanto		Monsanto		Monsanto	
Carrier Conc	2.2×10^{16}		2.2×10^{16}		2.2×10^{16}		2.2×10^{16}	
Mobility	2.3×10^{4}		2.3×10^{4}		2.3×10^{4}		2.3×10^{4}	
Type	n		n		n		n	
	Boule							
Carrier Conc				4.6×10^{16}		2.4×10^{16}	7.4×10^{16}	6.6×10^{16}
Mobility				1.8×10^{4}		2.2×10^{4}	1.8×10^{4}	2.1×10^{16}
Type				n		n	n	n
Crucible			SiO_2		SiO_2		SiO_2	

TABLE VI

SUMMARY OF GaP CRYSTAL GROWTH EXPERIMENTS

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate "/hr	Rotation Rate rpm	Encapsulant Depth cm	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
1	random	1.5	10	1.25	N_2	600→750	2 x 2 SiO_2	130	Boule polycrystalline from graphite starter. Columnar grains. Visibility extremely poor. Seal blew out during run allowing pressure to drop.
2	seeded	1.0	14	0.30	N_2	800	1-1/4 x 1-1/4 SiO_2	40	Boule polycrystalline. Run started cold. Apparently did not remelt back to seed. Large columnar grains. Good control of growth run.
3	seeded	1.0	14	0.80	N_2	800	1-1/4 x 1-1/4 SiO_2		Single crystal with one twin. Had surface spalls which caused internal cracking.
4	seeded	1/4	10	0.80	N_2	800	1-1/4 x 1-1/4 SiO_2	9.6	Polycrystalline after 1/2" of growth. Pressure dropped from 800→750 psig with loss of P. change from tail end of Gap-1 which was likely P deficient.
5	seeded	0.6	8	0.86	N_2	800	1-1/4 x 1-1/4 SiO_2	40.35	B_2O_3 opaque during run-could not see growth interface. Used finely crushed GaP powder as charge. Had poor control over diameter. Melt heated to 1300°C and had power failure. Charge soaked 14 hrs @ ~600°C prior to melting. Boule contained 3 or 4 grains at max diam (~7/8) all of which could be traced back to start. Boule had one large and one small grain at end of run.
6				0.7	N_2	800	1-1/4 x 1-1/4 SiO_2		Used premelted charge. B_2O_3 remained clear until melt cooled from 1590°C and then could not see through B_2O_3. Seed crystal continued to neck off so run terminated.

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TABLE VI (Continued)

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr.)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
7	-10° from <110>	1.0	8	0.9	N_2	800	1-1/4 x 1-1/4 SiO_2	34.3	Used charge from GaP-6 and scrap chips. B_2O_3 was not clear during run. Controller failed to operate and ran on manual. Polycrystalline boule covered by B_2O_3. Electrical contact on and working throughout run.
8	-10° from <110>	1/2-1.0	8	0.9	N_2	800	1-1/4 x 1-1/4 SiO_2	37.5	Used premelted charge. B_2O_3 not clean, poor visibility. Bicrystal boule grown. Both grains grew from seed. Electrical contact used throughout run.
9	-10° from <110>		8	1.0	N_2	800	1-1/4 x 1-1/4 SiO_2	38.5	Charge made up from boules GaP-4 and GaP-5. B_2O_3 not clear. Polycrystalline boule grown after much difficulty initiating growth. Electrical contact on throughout run.

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TABLE VII

CHEMICAL AND HALL ANALYSES OF GaP SAMPLES

(percent by weight)

	Raw Material		GaP-3		GaP-5		GaP-7	
Element	Dark Grains	Light Grains		Mid-Boule	Top	Bottom	Top	Bottom
B	VFT FT	VVFT						
Mg	VVFT VFT			VVFT				
Al	VVFT			VVFT		VVFT		VVFT
Si	VVFT VFT	VVFT		VVFT VFT		VVFT		VVFT
Ca	VVFT							
Cr	VFT							
Mn	VVFT							
Fe	VVFT VFT							
Ni	VFT							
Cu	VVFT							
Ga	H	H		H		H		
Pb				VVFT				
P	H	H		H		H		
	Raw Material							
Origin	Monsanto		Monsanto		Monsanto		Scrap	
Carrier Conc								
Mobility								
Type								
	Boule							
Carrier Conc				2×10^{15}		7.6×10^{17}		
Mobility				159		450	$\rho \sim 2 \times 10^{6}$ Ω cm	
Type				n		p		
Crucible			SiO_2		SiO_2		SiO_2	

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TABLE VII (Continued)

	GaP-8		GaP-9					
Element	top	bottom						
B								
Mg								
Al		VVFT						
Si		VVFT						
Ca								
Cr								
Mn								
Fe		VVFT						
Ni								
Cu		VVFT						
Ga		H						
Pb								
P		H						
	Raw Material							
Origin	Monsanto		scrap					
Carrier Conc								
Mobility								
Type								
	Boule							
Carrier Conc	$2.4\text{-}5.2\times10^{8}$							
Mobility	46-53		Not measured					
Type	n							
Crucible	SiO_2		SiO_2					

TABLE VIII

SUMMARY OF InP CRYSTAL GROWTH EXPERIMENTS

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr.)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
1	random	.95	8	0.60	N_2	320	1-1/4 x 1-1/4 SiO_2	47	Boule grown from graphite seed and was polycrystalline. Variation in thermal conductivity made necking difficult to control.
2	random	1/8	12		N_2	400	1-1/4 x 1-1/4 SiO_2		Columnar grained polycrystal. Seed sectioned for subsequent growth runs.
3	seed from InP-2	1/4	12	0.92	N_2	400	1-1/4 x 1-1/4 SiO_2	36.6	Large grained with substructure. Partial coverage of boule with B_2O_3.
4	seed from InP-2	1/8-1/4	8	1.27	N_2	400	1-1/4 x 1-1/4 SiO_2	14.6	Surface of melt dirty. Made up of small pieces from previous runs.) Large grained with substructure. Seed apparently established growth direction. Boule covered with B_2O_3.
5	seed from InP-2	1/4	8	1.1	N_2	400	1-1/4 x 1-1/4 SiO_2	36.0	Surface of melt remained clean throughout most of run. Islands evident on surface near end of run. Boule badly twinned. Boule covered with B_2O_3.

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TABLE IX

CHEMICAL AND HALL ANALYSES OF InP SAMPLES

(percent by weight)

	Raw Material		InP-2		InP-3		InP-4	
Element			Top	Bottom	Top	Bottom	Top	Bottom
Mg				VVFT VFT				
Al	VVFT			VVFT VFT	VVFT	VVFT		
Si				VVFT	VVFT	VVFT		
Ca	VVFT			VFT	VVFT			
Fe	VFT			VVFT				
Ga	VVFT							
In	H			H	H	H		H
Sb	FT							
P	H			H	H	H		H
	Raw Material							
Origin	Monsanto		Monsanto		Monsanto		misc. pieces	
Carrier Conc			$1.5x10^{16}$		$1.5-2x10^{16}$			
Mobility			$3-4x10^{3}$		$1.7-4x10^{3}$			
Type			n		n			
	Boule							
Carrier Conc				$6.7x10^{15}$	$2.3x10^{16}$	$3.0x10^{16}$		$3.0x10^{16}$
Mobility				$2.3x10^{3}$	$2.8x10^{3}$	$2.1x10^{3}$		$2.9x10^{3}$
Type				n	n	n		n
Crucible			SiO_2		SiO_2		SiO_2	

TABLE IX (Continued)

	InP-5							
Element	top	bottom						
Mg	VFT							
Al	VFT							
Si								
Ca	VVFT							
Fe	VVFT							
Ga	L-M							
As	T-L							
Ag	VVFT							
In	H							
P	H							
	Raw Material							
Origin	melt from InP-4							
Carrier Conc								
Mobility								
Type								
	Boule							
Carrier Conc	2.1×10^{16}							
Mobility	3.3×10^{2}							
Type	n							
Crucible	SiO_2							

TABLE X

SUMMARY OF GaSb GROWTH EXPERIMENTS

Boule No.	GROWTH PARAMETERS: Growth Direction	Growth Rate (in./hr.)	Rotation Rate(rpm)	Encapsulant Depth(cm)	Furnace Atm	Atm Pressure(psig)	Crucible	Boule Wt(gm)	Comments
1	<111>	1	32		N_2 & N_2/H_2	2→6	1-1/4 x 1-1/4 SiO_2		Thick, solid film formed on surface of melt upon melting and continued to build up over period of 24 hrs in N_2 atm. Film was not reduced in an additional 20 hrs in 50% N_2-50%H_2 atm. Polycrystalline boule pulled from melt.
2a				0.3	He/A	30	1-1/4 x 1-1/4 SiO_2		Film reformed on etched GaSb-1 boule. Began to go into solution in B_2O_3 @ 950°C, but viscosity of B_2O_3 increased and melt not clean after 20 hr. Change solidified.
2b	<111>	1/2	8	0.6	He/A	30	1-1/4 x 1-1/4 SiO_2	50	Melt remained clean with 3rd melting (2nd under B_2O_3). Single crystal grown.
3	<111>	1/3-1/2	8	0.7	N_2	12	#52 Vitreous Carbon	47	Melt made up from mixed ele Reacted without B_2O_3 encapsulant and formed solid surface film. Crystal grown from B_2O_3 encapsulated melt. Melt surface remained clear.
4	<111>	1/3-1/2	8	0.7	N_2	12	#52 Vitreous Carbon		GaSb-3 boule and remainder of charge remelted with B_2O_3 encapsulant. Melt surface remained clear.

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TABLE XI

CHEMICAL AND HALL ANALYSES OF GaSb SAMPLES

(percent by weight)

	Raw Material		GaSb-2		GaSb-3		GaSb-4	
Element			Top	Bottom	Top	Bottom	Top	Bottom
B								
Mg								
Al								
Si								
Ca								
Cr								
Fe								
Cu								
Ga								
Ag								
Sb								
Ba								
Pb								
	Raw Material							
Origin	Monsanto		Monsanto		ADL		ADL	
Carrier Conc	$2x10^{17}$		$1.6\text{-}3.0x10^{17}$					
Mobility	550		550					
Type	p		p					
	Boule							
Carrier Conc			$1.5x10^{17}$	$2.7x10^{17}$	$1.8x10^{17}$		$2.05x10^{17}$	$8.24x10^{16}$
Mobility			680	465	460		536	476
Type			p	p	p		p	p
Crucible			SiO_2		Vitreous Carbon		Vitreous Carbon	

TABLE XII

SUMMARY OF InSb CRYSTAL GROWTH EXPERIMENTS

	GROWTH PARAMETERS								
Boule No.	Growth Direction	Growth Rate (in./hr.)	Rotation Rate (rpm)	Encapsulant Depth (cm)	Furnace Atm	Atm Pressure (psig)	Crucible	Boule Wt (gm)	Comments
1	<111>	3/4	15		A		Vitreous Carbon		Some oxide on melt surface during run. One growth twin. Single crystal.
2	<111>	3/4	15		A		Vitreous Carbon		Oxide on melt surface throughout run. Polycrystalline.
3	<111>	3/4	15		A	22	Vitreous Carbon	22.1	Melt remained clean throughout run. No growth twins. Good single crystal.
4	<111>	1/2	10		A/He	8	1-1/4 x 1-1/4 SiO_2		Surface film on melt. Boule polycrystalline.

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TABLE XIII

CHEMICAL AND HALL ANALYSES OF InSb SAMPLES

(percent by weight)

	Raw Material		InSb-1d		InSb-3		InSb-4	
Element			Top	Bottom	Top	Bottom	Top	Bottom
B								
Mg					VVFT	VVFT		
Al					VVFT	VVFT		
Si					VVFT	VFT		
Ca						VVFT VFT		
Mn								
Fe						VVFT VFT		
Cu						VVFT		
Ga						VFT		
In					H	H		
Sb					H	H		
Pb					VVFT			
	Raw Material							
Origin			Mixed Elements		Monsanto		Monsanto	
Carrier Conc					$1.3\text{-}3.4\times10^{14}$			
Mobility					3.4×10^{5}			
Type					n			
	Boule							
Carrier Conc				7.3×10^{16}		7.2×10^{14}		
Mobility				3.4×10^{4}		1.4×10^{4}		
Type				n		n		
Crucible			Vitreous Carbon		Vitreous Carbon		SiO_2	

TABLE XIV

COMPARISON OF CHEMICAL ANALYSES BY JARRELL-ASH, BELL & HOWELL AND MONSANTO

	GaAs-8 Bottom				GaAs-11 Top			
Element	J. Ash Initial	J. Ash Recheck	Bell &* Howell	** Monsanto	J. Ash Initial	J. Ash Recheck	Bell & Howell*	** Monsanto
B	VVFT VFT	VVFT VFT	15	ND	ND	ND	1.4	ND
C	----	----	2.5	----	----	----	3.7	----
O	----	----	3.4	----	----	----	3.1	----
Mg	VVFT	VVFT	ND	.06	VVFT VFT	VVFT VFT	ND	.03
Al	VVFT VFT	VVFT	9.9	.01	ND	VVFT	15	.05
Si	VVFT VFT	VVFT VFT	0.3	.8	VVFT	VVFT	0.7	1.5
K	ND	ND	1.6	ND	ND	ND	1.6	ND
Ca	VVFT	VVFT	0.3	.5	ND	ND	0.3	.8
Fe	VVFT VFT	ND	ND	$\leq$.1	VVFT	VVFT	ND	.1
Cu	VVFT VFT	VVFT VFT	ND	.03	ND	ND	ND	.07
Ga	H	H			H	H		
Pb	ND	ND	ND	ND	VVFT	ND	ND	ND
Ag	ND	ND	ND	ND	ND	ND	ND	ND
Sn	ND	ND	ND	ND	ND	ND	ND	ND

*Bell & Howell ppm atomic

**Monsanto ppm by weight

TABLE XIV (Continued)

	GaAs-11 Bottom				GaP-8			
	J. Ash Initial	J. Ash Recheck	Monsanto		J. Ash Bottom	B & H MidBoule		
H						3.0		
Li						2.6		
B	VVFT	ND	ND			1.3		
C						1.6		
N						.96		
O						9.3		
F						7.2		
Na						.3		
Mg	VVFT	VFT	.06					
Al	VVFT VFT	ND	.2		VVFT	7.0		
Si	VVFT	VVFT	.3		VVFT	.28		
S						2.3		
Cl						.15		
K						.72		
Ca	ND	ND	.5			.88		
Fe	ND	VVFT	.2		VVFT			
Ni						.28		
Cu	ND	VVFT	.2		VVFT			
Ga	H	H			H			
Zn						.56		
Pb	VVFT	ND	ND					
As						8.0		
Ag	VFT	ND	ND					
Sn	VVFT	ND	ND					
P					H			

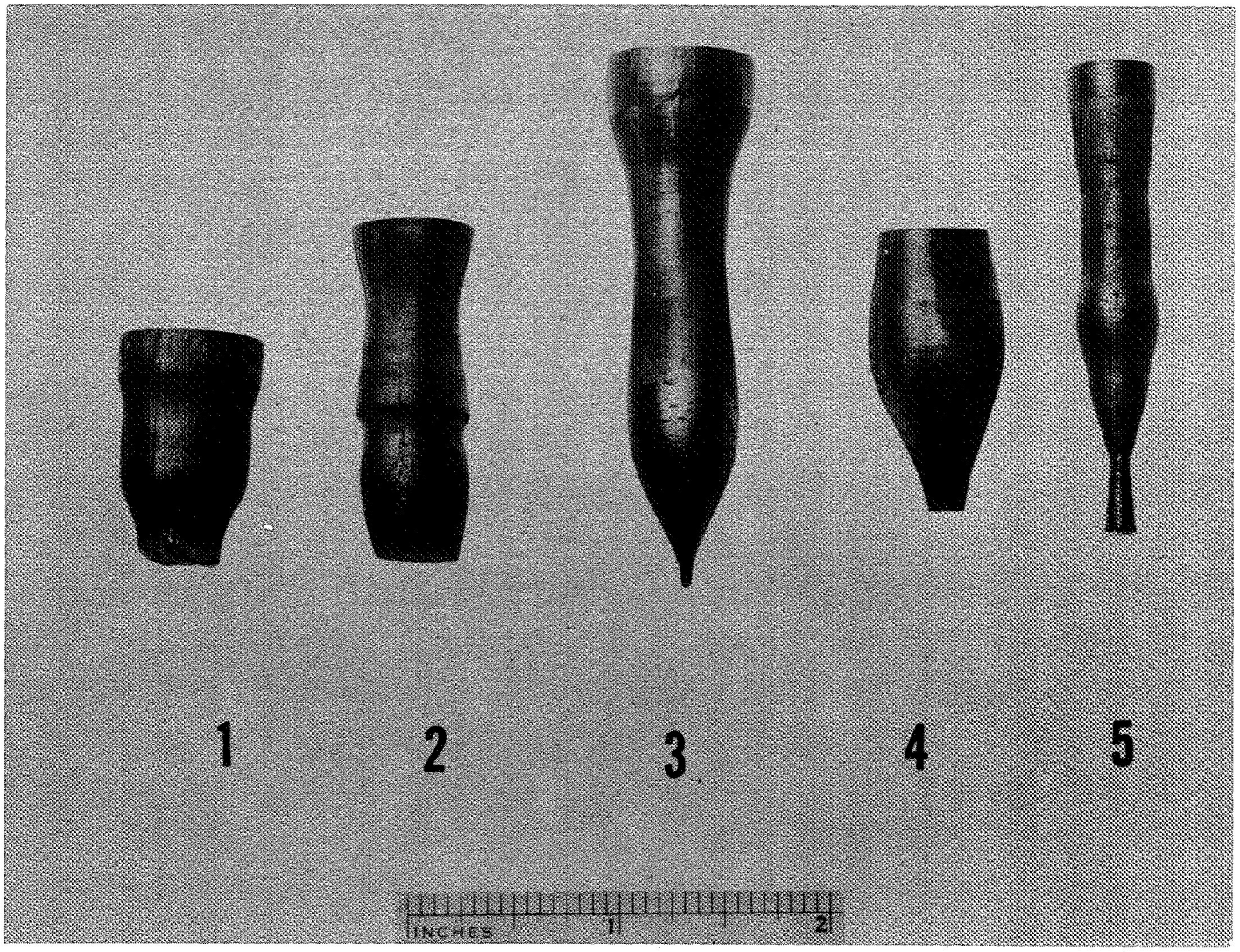

FIGURE 13 GaAs BOULES (1 - 5)
GROWN BY LIQUID - ENCAPSULATION TECHNIQUE

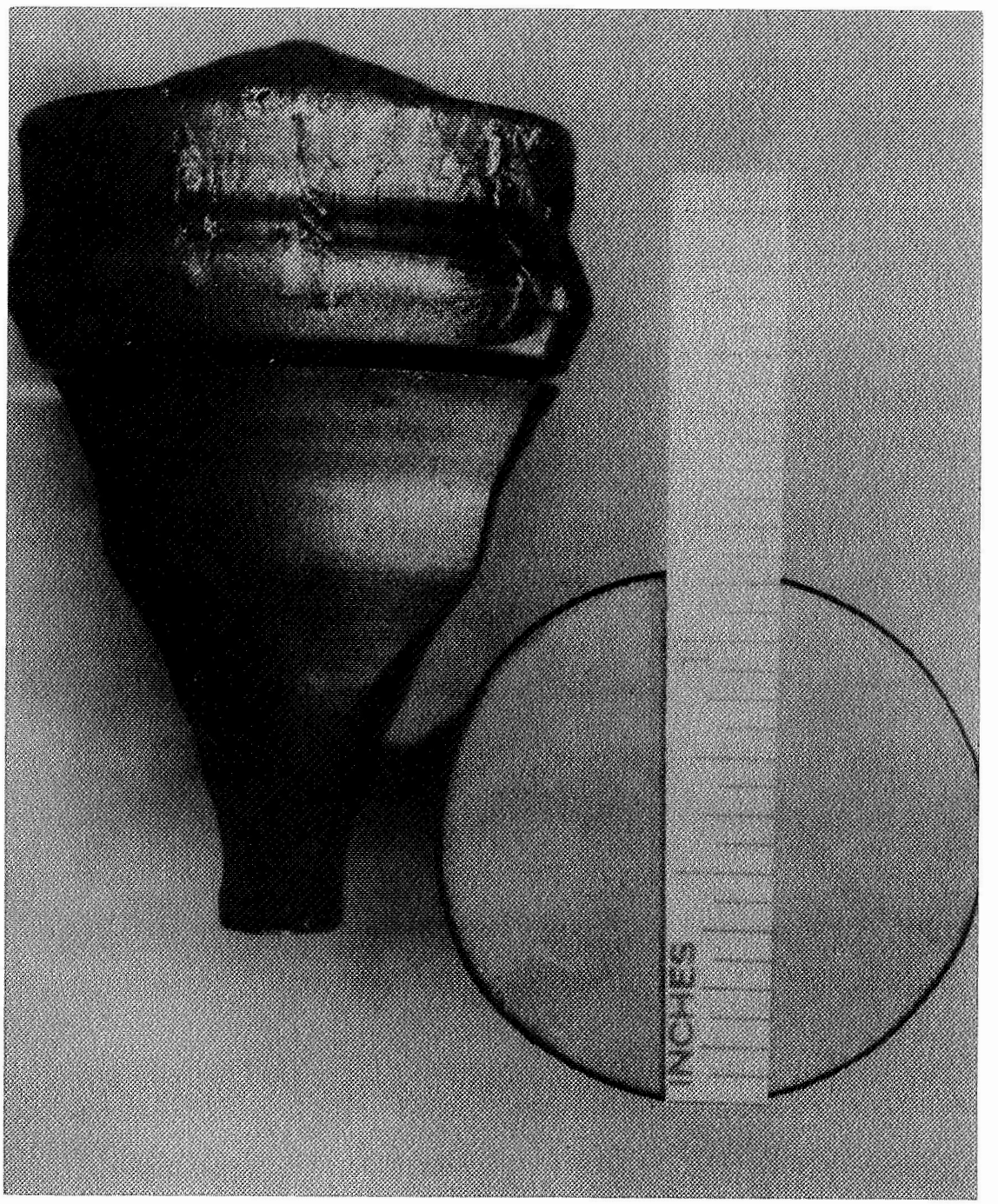

FIGURE 14 GaAs BOULE (10)
GROWN FROM A 2-INCH-DIAMETER CRUCIBLE

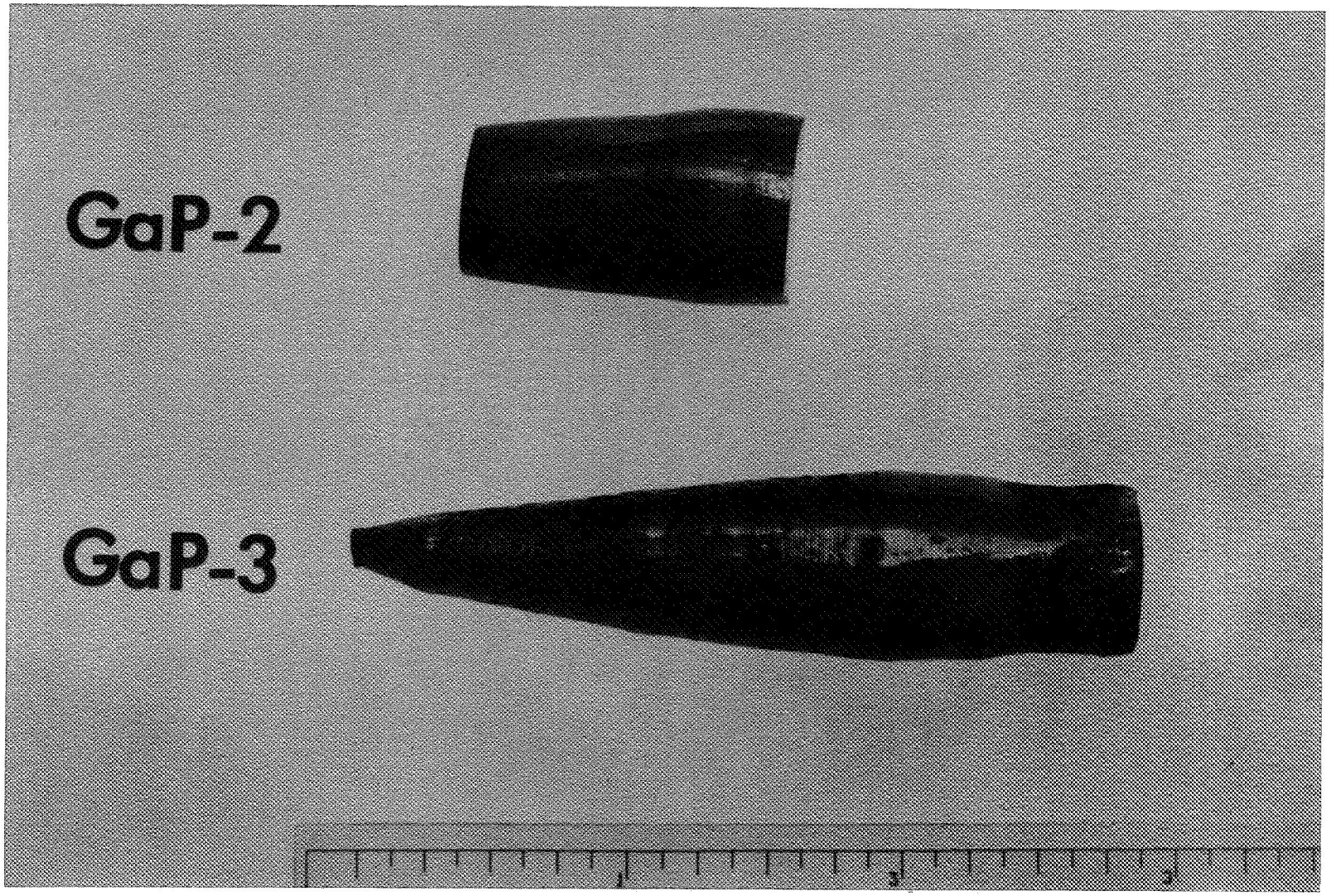

FIGURE 15 GaP BOULES 2 AND 3

GaP–2 IS A COLUMNAR GRAINED POLYCRYSTAL BOULE:
GaP–3 IS SINGLE CRYSTAL IN THE UPPER REGION AND
BY–CRYSTAL IN THE LOWER REGION

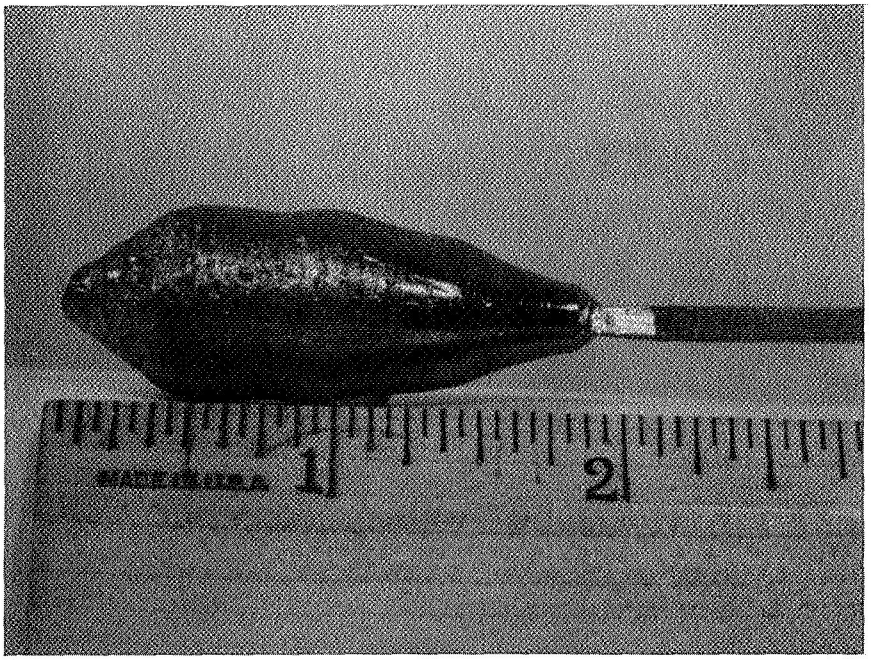

FIGURE 16 EQUIAXIAL GRAIN POLYCRYSTALLINE InP BOULE (5)

THE HIGH DEGREE OF CONTROL OF THE GROWTH PROCESS IS EXHIBITED BY THE SHAPE OF THE BOULE

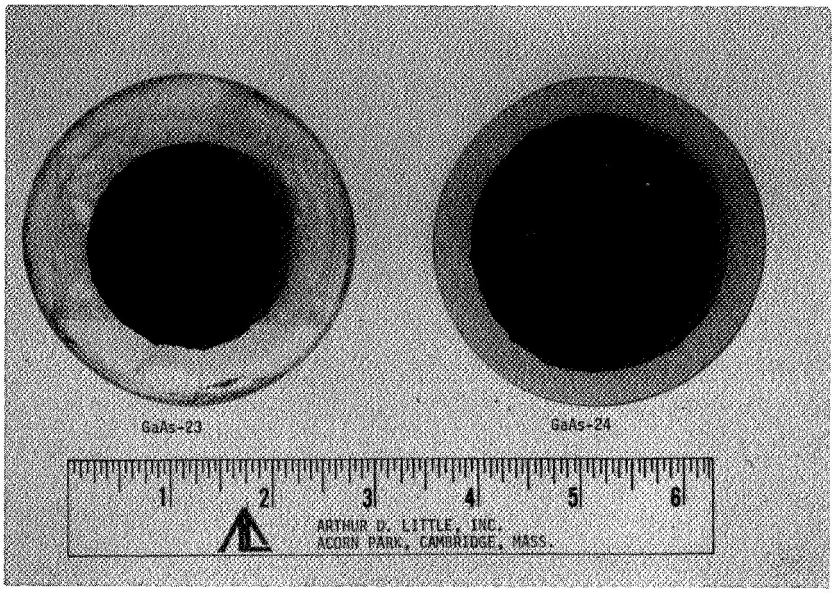

FIGURE 17 CROSS SECTIONS OF GaAs BOULES (23 AND 24) IN PLASTIC MOUNTINGS

GROWN BY THE LIQUID–ENCAPSULATED CZOCHRALSKI PROCESS FROM ADL–SYNTHESIZED MATERIAL

V. DISCUSSION OF CRYSTAL GROWTH EXPERIMENTS

A. GENERAL OBSERVATIONS ABOUT THE LIQUID-ENCAPSULATED CRYSTAL GROWTH TECHNIQUE

1. Evaluation as a Crystal Growth Process

Although the details of liquid-encapsulated growth of GaAs and InAs have been unusually well reported in the literature,[2] a number of detailed procedures had to be solved to make the process work satisfactorily for these materials, particularly for InP and GaP. A crucible-growth station had to be developed which would provide adequate visibility of the growth process throughout the entire growth run while inducing sufficiently steep temperature gradients above the crucible that would lead to coverage of the boules by the B_2O_3 encapsulant without degrading the quality of the crystals. Once satisfactory procedures were developed, the technique proved extremely flexible for producing high-quality crystals of a number of III-V compounds.

Crystals can be produced by this technique with equivalent or higher purity than that of the feed materials, provided the B_2O_3 is sufficiently pure, the time at temperature is short, and materials handling procedures are correct. Surprisingly little boron (concentration generally less than 1-10 ppm by weight) is introduced from the B_2O_3. The growth rates used (up to 1.5 inches per hour) are high compared to those reported for hot-wall autoclave processes and orders of magnitude larger than those used for single crystal growth from solvents. The diameters of crystals are limited only by the diameter of the crucibles and size of the charges used. The 2.5-inch-diameter crystal (GaAs-24) is the largest diameter crystal of this compound with which we are familiar. The 3/4- to 7/8-inch diameters of GaP crystals 3 and 8 were the largest at the time of their growth. Since then, 300 gm GaP single crystals with diameters in excess of 1-1/2 inches have been grown (Bell Telephone Laboratories, Murray Hill, N. J.) in an ADL High-Pressure Crystal Growing Furnace. These were grown by the liquid-encapsulated Czochralski process using

some of the procedures developed in this program. These results indicate that the process has a number of advantages over the hot-wall autoclave process for producing single crystals of the arsenides and is clearly superior for synthesis of the phosphides.

The B_2O_3 encapsulant was used both with InSb (InSb-1d) and GaSb (GaSb-2b, 3 and 4) melts to dissolve non-volatile solid films which formed on their surfaces. The liquid-encapsulation crystal growth process is useful not only for controlling the loss of volatile constituents from contained melts but for upgrading the quality of III-V melts.

As pointed out in an earlier section, crystal growth can be carried out directly after synthesis of a stoichiometric melt under a B_2O_3 encapsulant. This technique offers potential economic and material quality advantages over the typical two-step, vapor-phase reaction and hot-wall Czochralski Crystal Growth processes used for the arsenides. If procedures were developed for the phosphides, a significant improvement in quality could be expected since the porous sponge, with its high surface area, would not be contaminated.

2. Thermal Etching of Arsenide and Phosphide Boules

The surfaces of GaAs, InAs, GaP and InP boules were degraded after growth both when covered and when free of the B_2O_3 encapsulant: but by different mechanisms. When the boules are covered by a thick layer of B_2O_3, chips were spalled from the boule surface because of the differences between the thermal expansion coefficients of the crystal and the B_2O_3 glaze. The damaged layer usually extended more than 2 mm into the boule. Occasionally, cracks originating at the surfaces propagated across the boules. In general, the thicker B_2O_3 glazes resulted in more extensive damage. When the axial temperature gradient in the crystal was reduced to such a degree that the B_2O_3 flowed off the boule completely, considerable thermal etching occurred by preferential vaporization of As or P. The degradation caused by thermal etching does not extend as deeply into the boule as that caused by spalling and this was originally considered a better condition under which to grow crystals of these compounds. Later it was observed that gallium freed by the loss of arsenic

and phosphorus would accumulate on the surface of boules until it ran down to the growth interface and caused the boules to twin. Thermal etching of the boules should be minimized to insure reliable single-crystal growth.

The temperature gradient above the surface of the III-V melt and the encapsulant thickness determined the degree of coverage of the crystals. The temperature at the encapsulant-boule-gas interface must be low enough to increase the viscosity of the B_2O_3 sufficiently to keep the B_2O_3 from running off the boule. This condition can be achieved either by inducing a steep temperature gradient in a thin encapsulant layer or by using a thicker encapsulant layer in a shallow gradient. Increased ambient pressures have been observed to promote coverage of the boule by B_2O_3; presumably the increased heat capacity of the ambient gas increased the temperature gradient in the boule. Coverage was more readily achieved with vitreous carbon and pyrolytic BN crucibles than with fused silica crucibles. This better coverage probably resulted because the first two types transmit less heat to the boules from the graphite susceptors than do the silica crucibles.

Heavy coverage of the boules does not appear necessary for reducing thermal etching to satisfactory levels; however, achieving conditions in which GaAs boules remain covered with only a very thin layer of B_2O_3 required a number of variations of rf coil configurations, susceptor positions, ambient atmospheres and encapsulant depths. When vitreous carbon or pyrolytic BN crucibles are used, this condition is achieved for GaAs with the upper edge of the susceptor shown in Figure 5 positioned 3/16" above the upper turn of the rf coil (Appendix D) in a N_2 atmosphere at 15 psig with a B_2O_3 encapsulant depth of 0.75-0.85 cm. When a fused silica crucible is used, conditions are the same as for GaAs except that the susceptor is positioned 5/16" above the upper turn. Similarly detailed conditions for minimal coverage of crystals of the other compounds have not been established, but they were in fact usually covered by B_2O_3. Indium arsenide (MP = 942°C) and indium phosphide (MP = 1062°C) melt sufficiently lower than GaAs (MP = 1237°C) that the B_2O_3 does not run down off the crystals. The high pressure (800 psig) required for growth

of gallium phosphide (MP = 1450-1500°C) apparently caused sufficient cooling of the crystal to compensate for the increased melting point.

Hydrogen-argon mixtures were used in several growth runs to suppress arcing in the pure argon atmosphere. The presence of hydrogen in the furnace during crystal growth strongly accelerates thermal etching of GaAs under conditions when the boules are not covered or only thinly covered by B_2O_3. The acceleration of thermal etching in the presence of hydrogen very likely results from the formation of arsene (AsH_3) gas.

B. CHEMICAL ANALYSIS

Samples taken from two GaAs crystals and one GaP crystal (GaAs-8 and 11 and GaP-8) were resubmitted to Jarrell-Ash Co. and submitted to Monsanto Co. and Bell and Howell for emission and mass spectrographic analyses, respectively. These analyses were made in an attempt to explain the unlikely and highly variable impurities reported by Jarrell-Ash Co. The mass spectrographic characterization technique also indicated levels of many important impurities not obtainable by emission spectrographic techniques, e.g., C, N_2, O_2. The results of these duplicate analyses, as well as the original Jarrell-Ash analysis, are given in Table 14.

Clearly the improbable impurities (Pb, Ag and Sn) originally reported by Jarrell-Ash were not characteristic of the samples and were introduced by improper handling procedures. As far as can be determined, the only difference between the original and rechecked sample preparation procedures was that the rechecked samples were not powdered at Jarrell-Ash prior to analysis. Emission analyses were made of bulk samples in the case of the rechecks. Special techniques, which were not employed by Jarrell-Ash (and presumably Monsanto), are needed to detect low levels of K by emission spectroscopy. The other differences between the levels of probable impurities (Mg, Ca, Fe and Cu) appear to point out the differences between the sensitivities of spark-source and emission spectroscopy. The Monsanto analyses generally agree with the repeated Jarrell-Ash analyses. The only major unexplained inconsistency between these results is in the reported Al levels.

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C. SPECIFIC MATERIALS

1. B_2O_3

Two kilograms of high-purity B_2O_3 (two separate lots) were purchased from the British Drug House, Poole Dorset (England) during the program for use as liquid encapsulant. This source offered the highest purity B_2O_3 commercially available. Purities of 99.99^+ were claimed and the material was particularly low in Group II elements, which are electronically active in III-V compounds.

Our analysis of the material shipped from the first lot, Table 1, showed Fe and Mg to be present at levels between 0.001 and 0.01 percent by weight. Both generally act as acceptors in the compounds of interest. (4)

The second kilogram of material was ordered under the condition that the lot would by analyzed to insure that it met specifications prior to shipment. Our analysis of the second lot of material, Table 1, showed the material met advertised specifications as well as the analysis of that specific lot. Evidently the second lot of material is substantially purer than the first one. The trace level of aluminum was probably introduced from the aluminum containers in which the material was shipped. (The first lot was shipped in glass containers.)

The analyses of B_2O_3 samples before and after degassing showed that impurities were not introduced into the B_2O_3 during the drying process. After they were dried, both samples showed an apparent increase in Si content. No reason is known for its occurrence.

Several lumps of B_2O_3, taken from the first lot of material in the as-received condition, were analyzed. Different lumps of material showed either no trace of Fe or levels of approximately 0.010%. Samples taken from several lumps were dissolved in high-purity water and the water removed to produce a sample with an averaged iron content. This sample contained 0.001-0.010% Fe by weight. Sufficient analyses were conducted to show that the variable impurity levels did not result from surface contamination of the samples, as first suspected, but from a nonhomogeneous distribution of contaminants.

2. GaAs

Gallium arsenide was used as the lead material in this program of developing liquid-encapsulated crystal growth. The vapor pressure at its melting point (approximately 1 atmosphere) does not require remote operation and thus permits maximum visibility of the process. Its melting point is the second highest of the six III-V compounds considered in the program. Material transport rates, reaction rates, and failures of the furnace system are influenced far more strongly by increased temperatures than by ambient pressures of inert gasses; thus, GaAs was considered the best material to test the reliability and inertness of the furnace system and crystal growth station for liquid-encapsulated crystal growth.

During this program 24 gallium arsenide crystals were grown and most were characterized chemically and electrically. The first eight boules were grown with material purchased from the Monsanto Co. and the latter from scrap material purchased from Bell & Howell, or ADL synthesized material.

All GaAs crystals produced were grown along the <111> direction away from the A face in the polar zinc-blende structure. Initial seed stock was purchased from the Monsanto Co. (St. Louis, Missouri). Seeds could be reused without degradation unless inadvertently melted back too far during the start of a crystal growth run. Growth rates generally were between 1 to 1.5 cm per hour on the boules that were characterized (Table 2). Growth rates in this range permit an entire growth run to be completed in 6 to 10 hours from initial melt down. Higher growth rates, up to 3 cm per hour, were used on other boules which solidified as single crystals. Temperature adjustments to control the shape of the boule, had to be made in smaller increments at the higher growth rates to avoid twinning. A pulling rate of 0.6 cm per hour was used for the 1-3/8-inch diameter boule GaAs-10 giving a true growth rate of approximately 1 cm per hour. When thermal etching of the boules was minimal, growth of GaAs single crystals was quite straightforward over a wide variety of growth rates. It is not necessary to grow crystals from fine, long necks if

reasonable quality seeds are used to initiate growth, although it has been found that slightly undercutting the seed prior to initiating growth increases the probability of the seed establishing the growth direction.

Faceting was evident on the surfaces of GaAs boules grown parallel to a <111> direction, especially on regions of crystals having diameters between 0.5 and 1.0 cm. The boules tended to assume an equilateral triangular morphology, but poles of the facet planes were not identified further.

With the exception of GaAs-13, the net balance of electrically active impurities in the crystals became increasingly p-type along the boule. If the first region to solidify was n-type, subsequent portions of the boule contained lower levels of excess electrons and usually exhibited increasingly p-type behavior by the end of the boule. This behavior demonstrates the presence of both donor and acceptor impurities with different distribution coefficients or the introduction of a p-type impurity during or after the crystal growth run.

The Chemical and Hall analyses of representative crystal samples do not identify the impurity(s) responsible for the electrical properties and are, in fact, difficult to explain satisfactorily on the basis of published distribution coefficients of probable dominant impurities.

The range of carrier concentrations observed for p-type crystals was far narrower than for n-type crystals: hole concentrations varied approximately two orders of magnitude (3.8×10^{14} to 4.3×10^{16} per cm^3) while excess electron concentrations varied more than eleven orders of magnitude (1.8×10^{7} to 4.8×10^{18} per cm^3). In addition, in crystals which exhibited p-type behavior over their entire lengths (GaAs-2, 8 and 22), the carrier concentration varied only 3.6 to 6.3 times, far less than the variations in excess electron concentrations.

The uniformity in the p-type behavior can be explained by a distribution coefficient in the range of 0.2 to 0.5.[8] The dominant n-type impurity(s) must have a higher distribution coefficient to explain switching from n-type behavior in the "first to solidify" region to

p-type behavior in latter portions of the boule solely on the basis of segregation of impurities. Silicon, which is usually the dominant impurity in n-type GaAs synthesized in hot-wall SiO_2 reactors, has a distribution coefficient of 0.1.[5] It is unlikely that it was the dominant impurity, because the distribution coefficient is lower than the apparent distribution coefficient of the dominant p-type impurity. Also, the excess electron concentrations in purchased feed materials were generally in the low 10^{16} per cm^3 range so the Si content in the "first to solidify" region would be lower than the carrier concentrations generally observed (providing dominant impurity in the feed material was Si).

Magnesium is the only donor impurity[4] identified in the GaAs crystals which has a distribution coefficient greater than 0.2.[5] The quantitative emission spectrographic analyses made by Monsanto indicate a Mg content between 0.03 and 0.06 ppm by weight, or approximately 3.7×10^{15} to 8×10^{15} per cm^3. This is the correct order of magnitude to explain the observed effects, but it would be presumptuous to present it as the dominant donor impurity.

Copper and iron are two acceptor impurities consistently indicated as impurities at the levels approximating the observed carrier concentrations (1 ppm by weight of Cu $\approx 5 \times 10^{16}$ per cm^3 and Fe $\approx 5.7 \times 10^6$ per cm^3 in GaAs). However, their distribution coefficients ($\approx 10^{-3}$) are too low to be consistent with the results unless they were introduced to the melt continuously during the crystal growth process or their diffusion through the crystal was rapid. It is again impossible to identify the dominant p-type impurity(s) in these GaAs crystals with any certainty.

More complete characterization of the boules is required to clarify these important questions.

The room-temperature mobilities of both p-type (up to 640 $cm^2/v\text{-sec}$) and n-type (up to 5.7×10^3 $cm^2/v\text{-sec}$) boules show that high crystallographic quality can be achieved by this growth technique. The hole mobility observed in GaAs-4 exceeds, by almost a factor of two, the best value reported up to 1961.[6]

Etch-pit counts of dislocations also show the crystals to have a high crystallographic quality. The photomicrograph shown in Figure 18 indicates that approximately 2.5×10^4 dislocations per centimeter are present in the as-grown GaAs crystals. The dislocations do not appear concentrated in low angle boundaries but are distributed fairly uniformly across the samples. Schulz x-ray topographical photographs of GaAs samples also show no detectable substructure.

At an ambient gas pressure of 75 psig, films formed on the surface of GaAs melts 1, 2 and 3. In a brief literature survey it was found that Ga is transported via the vapor phase as Ga_2O in the presence of extremely low partial pressures of water.[7] It was postulated that residual water in the B_2O_3 might react with GaAs to form Ga_2O, H_2 and As (possibly AsH_3). The latter vaporized while the Ga_2O went into solution in the B_2O_3 glass up to its solubility limit. Further oxidation of the GaAs resulted in the formation of an oxide film that was prevented from vaporizing under the high ambient furnace pressures. Melt 4 was grown under an ambient pressure of 15 psig and the surface remained clean throughout the run. Melt 5 was made up from scrap and the surface was partially covered by a film at an ambient pressure of 15 psig. Bubbles were observed to form at the patches of the surface film when the pressure was reduced to 8 psig. The melt cleared completely at 4 psig by apparent vaporization of the surface film. Subsequently, the drying procedures for the B_2O_3 were improved and the GaAs melts generally remained free of a surface film with ambient pressures up to 20 psig.

A significant difference was observed in the boron contents in GaAs crystals, depending on the crucible material used. A crystal grown from a vitreous carbon crucible, GaAs-8, contained approximately ten times the boron level as one grown from a high-purity, SiO_2 crucible, GaAs-11 (Tables 3 and 14). The other spectrographic analyses, Table 3, generally support this observation. Crystals grown in BN crucibles were not analyzed quantitatively. Spectrographic analysis of the vitreous carbon crucible, Table 1, does not indicate the presence of boron. No explanation has been identified for this effect. It would be anticipated that

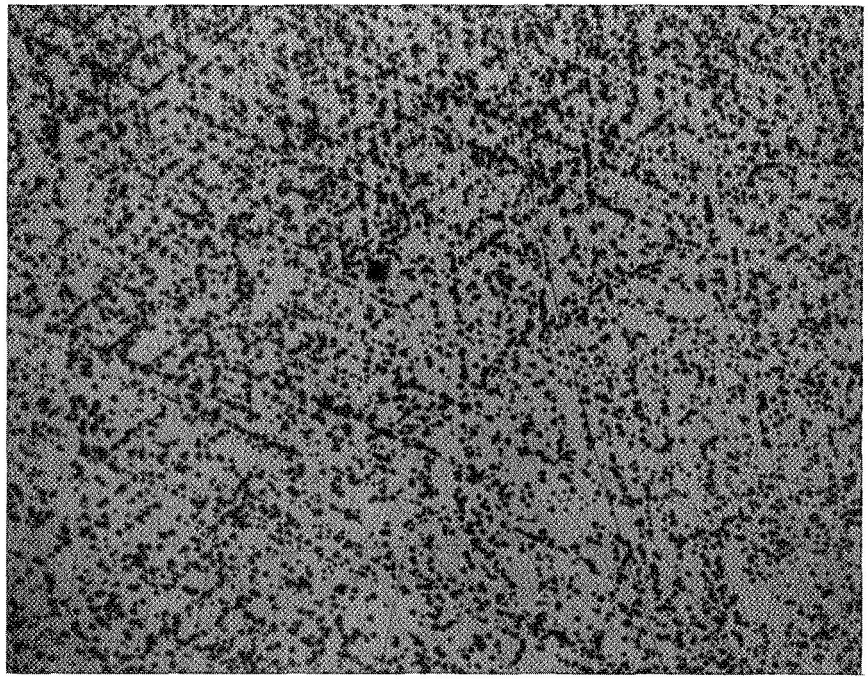

FIGURE 18 DISLOCATION ETCH PITS ON A <111> PLANE OF GaAs–8
THE DISLOCATION CONTENT IS APPROXIMATELY 2×10^4 per cm^2. MAGNIFICATION 22X.

the boron impurity may adversely affect carrier mobilities at the higher impurity levels; however, this is not supported by the Hall characterizations.

Two GaAs single crystals (GaAs-20 and 22) were grown from ADL synthesized material. The charge used for GaAs-20 was the first material successfully synthesized. It had been melted and leached from crucibles four times prior to its use in a crystal growth run, so it is likely that some contamination occurred. It was also somewhat off stoichiometry, which caused the GaAs-20 boule to twin. The carrier concentration was higher than most of the crystals grown from commercial feed materials, but the electron mobility was comparable. The GaAs-22 boule was grown from material made in the final synthesis run. Improved handling procedures are reflected in the quality of GaAs-22. The carrier concentration and hole mobility in the top of the crystal are equivalent to the best GaAs crystals grown during the program. Both carrier concentration and hole mobility degraded somewhat at the bottom of the boule.

The elemental gallium and arsenic used for the synthesis and crystal growth runs were not maximum purity (approximately 99.999%) so it is highly probable that the quality of crystals grown from material synthesized under an encapsulant can be improved. Also, it appeared entirely feasible to grow crystals from melts directly after synthesis without further handling of the reacted charges. This should also improve the crystal quality. Although these crystal growth experiments could not be pursued, it is clear from these results that high-quality crystals can be produced by a one-step-synthesis-growth technique. The combination of encapsulated Czochralski crystal growth with an optimized synthesis cycle should permit significant reduction in the cost of producing GaAs single crystals.

Two large-diameter GaAs boules (GaAs-23 and 24) were grown to demonstrate the feasibility of using the liquid-encapsulated process to grow GaAs crystals with diameters greater than two inches. The cross sections of the boules, Figure 17, show that GaAs-23 was at least two inches in diameter and GaAs-24 was at least 2-1/2 inches in diameter. Both boules were grown from 3-inch-ID, SiO_2 crucibles from approximately

500 gm charges. The charges were made up of residual charges from previous runs, polycrystalline boules, and ADL synthesized material. The seed broke during the growth of GaAs-23 dropping the boule into the melt; however, the power was turned off before the boule remelted. The section shown in Figure 17 was salvages from the solidified boule and melt. The GaAs-23 boule was twinned and cracked so it and the remaining charge were remelted for the GaAs-24 growth run. The GaAs-24 boule was also twinned and cracked but at lower levels than GaAs-23. The twinned structure resulted from the melt being off stoichiometry. This was evident both from the nature of the growth run and the excess gallium in the residual charge. Elimination of cracking will probably require modification of the thermal environment surrounding the growing crystal.

These boules demonstrate that the liquid-encapsulant Czochralski growth process is amenable to producing large-diameter crystals. As with the growth of any large diameter, refractory crystal, thermally induced stresses must be controlled carefully to produce crack-free, low-dislocation-content crystals. There is no apparent reason why this control cannot be accomplished, and materials losses during device fabrication reduced, and the dimensions of IR optic elements increased substantially.

3. InAs

Four indium arsenide growth runs were made during this contract. The growth parameters are summarized in Table 4 and characteristics of resulting crystals in Table 5. The spectrographic analysis of the raw material purchased from Monsanto shows the InAs to be approximately the same purity as its GaAs.

The electrical characteristics of the samples tested show that all of the crystals had equal or higher concentrations of excess electrons than the feed material; mobilities are approximately the same. It is not apparent from the spectrographic analyses whether the increased excess electron levels result from the loss of acceptors or contamination by donors. The apparent impurity levels in the crystals are essentially

equal to each other and to the starting materials within the error of the analyses. A possible exception is an increased Si content. InAs-2 was grown after the charge had been molten for 12 hours; InAs-3, 6 hours; and InAs-4, 28 hours. The electron excess clearly increases with time and we believe it results from contamination of the charge by the SiO_2 crucibles.

Growth runs were seeded in the <111> direction away from the A face. Some problems were encountered with a surface film on the melts but they were cleared either by soaking for long periods or freezing and remelting the surface of the charge. The boules remained covered by a B_2O_3 film which prevented thermal etching.

4. GaP

Nine crystal growth runs were made with gallium phosphide. Growth parameters are summarized in Table 6 and the results of chemical and Hall analysis in Table 7. The number of GaP crystal growth runs does not reflect the intense interest in the material; however, they were limited by the furnace time required to satisfy the entire scope of work. The High Pressure MP Furnace was used extensively with InP.

The seals on the upper push rod developed leaks during the GaP-1 and -4 growth runs. Phosphorus vapors apparently diffused past the felt wiper and scraper plate in the gland assembly where they attacked the O-ring. Subsequent runs were made with a water-cooled shaft so phosphorus condensed onto the shaft allowing the scraper plate and felt wiper to function properly. No pressure leaks developed after this modification.

The growth process was substantially less visible with GaP than with other materials because of the combined effects of the poorer contrast achievable with black and white TV (required for remote operation) compared with direct observation, distortions from convective gas flow in the chamber, and a tendency of the B_2O_3 to become opaque after the GaP melted. The reduced visibility was the major problem encountered in the growth of GaP single crystals.

The B_2O_3 encapsulant remained clear throughout entire crystal growth runs with GaAs, InP and GaSb. However, the encapsulant became, and generally remained, opaque soon after the GaP charge melted. When powders were used for GaAs charges, particles of GaAs became suspended in the B_2O_3 and it became opaque. This effect was undoubtedly partially responsible for the opaqueness of the encapsulant in the first five GaP growth runs since the charges were made up from a porous sponge (Monsanto).

Subsequent GaP charges were densified by premelting and the crystal growth run was made with a fresh encapsulant. These encapsulants also became opaque but to a lesser extent. The encapsulant used with GaAs became completely opaque after cooling at the termination of a growth run. At room temperature, the glass was found to be two-phase. Apparently, the B_2O_3 used for GaAs became opaque because of phase separation after a solubility limit was exceeded upon cooling. A similar effect may have also been responsible for the opacification of the encapsulants used for GaP since these charges were superheated approximately 100°C during initial melting even though melts of other materials were superheated this much without the B_2O_3 becoming opaque upon subsequent cooling to growth conditions. This implies that the B_2O_3 encapsulant becomes saturated more quickly with GaP, which is reasonable since the melting point of the GaP is the highest of the materials investigated and diffusion coefficients increase exponentially with temperature.

The opaqueness of the B_2O_3 seriously impaired control of the growth process, particularly during the seeding step. The electrical contact, described in Section III, was used to indicate when the seed contacted the melt and thereby partially overcame the poor visibility.

No GaP single crystals were available commercially at the initiation of this program for use as seeds. GaP-1 was grown from a graphite starter rod after necking the boule to approximately 1/8" diameter. Several grains penetrated the necked region of the boule, and the lower region contained large columnar grains. These grains were sectioned from the boule for seed stock.

Gallium phosphide showed very little evidence of a preferred growth direction or a tendency to twin. Virtually all of the grains in

polycrystalline boules could be traced to the necked region of the boule when graphite starter rods were used or to the vicinity of the seed when improperly seeded. "Cold starts" occurred when inadequate visibility prevented undercutting the seed prior to initiating growth. The seeds were completely effective in establishing the growth of GaP-3 and -8. The upper portion of GaP-3 was monocrystalline and the GaP-8 was a bicrystal. The seed used for GaP-8 was inadvertently melted back into a bicrystalline region, and both grains were grown into the boule.

All of the GaP boules have been at least partially, and usually completely, covered with the B_2O_3 encapsulant. There was essentially no degradation of the boules by thermal etching under the growth conditions used. Boule GaP-2 was covered with a sufficiently thick layer of the encapsulant that the surface was spalled and some cracks propagated into the boule from the surface chips.

It was noticed that the color of individual grains in the polycrystalline sponge feed material (Monsanto Co.) varied. The majority were light orange but some ranged from dark red to black. Spectrographic analysis of the two types of grains, Table 7, showed that the light grains were substantially purer than the dark grains.

The results of the Hall characterization, emission spectrographic analyses and mass spectrographic analyses are in poor agreement, Tables 7 and 14. The emission spectrographic analyses (Jarrell-Ash) indicate that the GaP crystals were the purest materials produced during the program. Hall characterization of boules GaP-3 and -8 are in general agreement with this conclusion while GaP-5 apparently contains active impurities not detected by emission analysis. The mass spectrographic analysis (Bell & Howell) showed that GaP-8 was, in fact, quite impure; it contained many elements not detected by emission spectrographic analysis. Based on numerous analyses of other samples, it is believed that with the possible exception of carbon, the impurities in the crystal resulted from impurities in the feed material rather than handling procedures.

The electrical behavior of these impurities in GaP is not well documented in the literature; however, it would be extremely fortuitous for

all these impurities to compensate for one another leaving only approximately 10^8 carriers per cm^3. It is more likely that one or more act as a deep level trap and compensate for the majority of the impurities. The carrier concentration was relatively uniform in the boule.[9]

The high concentration of oxygen in these crystals probably resulted from internal oxidation of the high-surface-area, porous, polycrystalline sponge feed material. Synthesis of the compound directly from high-purity elements should be particularly effective in improving the purity of GaP single crystals.

The quality of these GaP crystals was not as uniform as crystals of the other compounds grown during the program; however, the carrier mobilities in crystals GaP-3 and -5 show that good crystals can be grown by the liquid encapsulated Czochralski technique. The variability resulted both from the difficulty of remote crystal growth operation and from the probable variable quality of feed materials. Schulz x-ray topography showed no evidence of substructure in the crystals.

Contacts for Hall measurements on high-resistivity GaP samples proved extremely difficult to make. Most of the room temperature Hall measurements on GaP samples were made by C. Kellett, NASA/ERC.

Although GaP crystal growth experiments could not be pursued as far as desired during the program, this work formed the basis for the growth of high-quality GaP single crystals up to 400 gms in weight in an ADL High Pressure Model HP crystal growing furnace. The growth techniques developed are sound; however, more growth experiments are required to optimize growth procedures.

5. InP

Five InP boules were grown by the Czochralski technique during this program. The growth parameters are summarized in Table 8 and both chemical and Hall analyses are given in Table 9.

Growth of InP single crystals proved to be elusive. Seeds were sectioned from large-grain regions of InP-2 but they were ineffective in establishing the growth direction and monocrystalline solidification.

The grains in InP-4 and -5 were equiaxed rather than columnar. This type of microstructure results from nucleation occurring ahead of the growth interface. Constitutional supercooling or fracture of dendrites are the mechanisms by which equiaxed structures are produced.

Metallographic analysis of InP boules 2 and 5 indicated the presence of a second phase which was present at sufficiently high levels in the lower end of InP-5 to be detected by x-ray diffraction techniques. It was identified as free indium. Subsequent metallographic analysis of the feed materials (Monsanto ingots 11 and 18) showed that they were also two-phase. Some grains in InP ingot 18 contained 20-30 volume percent of the second phase. It was concluded that the equiaxed polycrystalline microstructures result primarily through solidification from phosphorus-deficient melts.

Spurious surface nucleation was also a contributing factor to the solidification of polycrystalline boules. A film was observed on the surfaces of some InP melts. A similar film was the cause of polycrystalline solidification in GaAs, InSb, and GaSb and was believed to be a surface oxide which forms by reaction either with dissolved water in the B_2O_3 or with oxygen introduced to the system as an impurity in the gas or the charge. No InP Czochralski crystal growth runs were made since improved drying procedures for the B_2O_3 were developed.

Five unidirectional solidification (vertical Bridgman) runs were made with InP melts at slower solidification rates than are practical for Czochralski growth. The goal of these Bridgman runs was to produce stoichiometric InP segregating the excess In from the melts. Solidification rates of approximately 2 mm per hour were used in these 60-hour runs. These runs were made in a single 2-1/2-inch long x 1/2-inch ID, pyrolytic BN, pointed bottom crucible (Union Carbide Co.).

The degree of segregation and the shape of the solidification interface are shown clearly in Figure 19. The convex shape of the solidification interface shows that the heat losses from Bridgman growth apparatus, Figure 9, were conducive to single crystal solidification. Some phosphorus was lost during the solidification runs so the initial

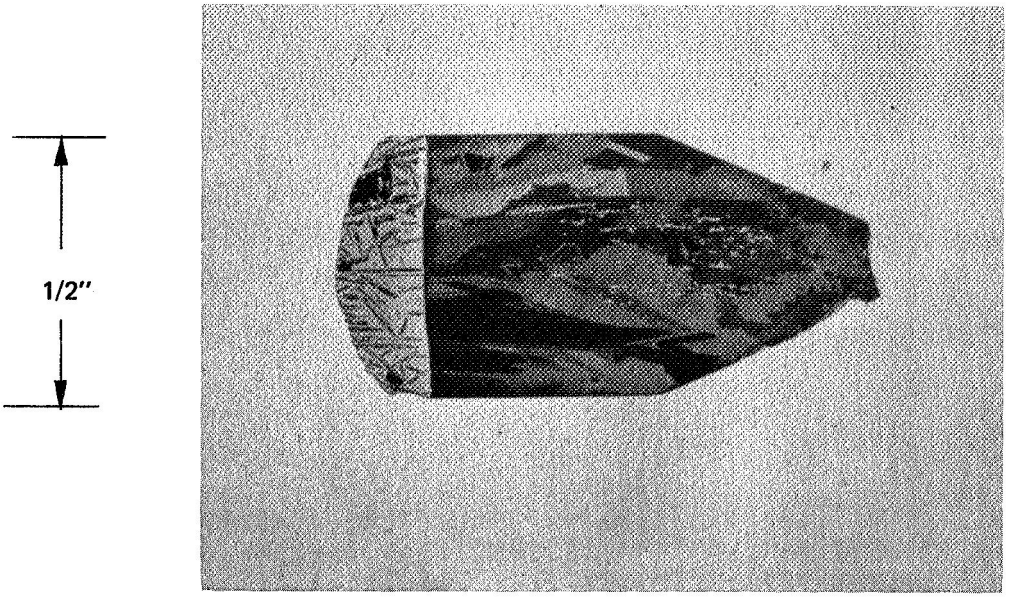

FIGURE 19 AXIAL CROSS SECTION OF BRIDGMAN SOLIDIFIED InP BOULE

phosphorus deficiency of the melts was not as high as implied in Figure 19. Most of the phosphorus was lost prior to melting the InP when the B_2O_3 percolated down through the charge, exposing InP lumps at the top of the crucible.

The first four runs were made with charges made up from the InP boules grown by the Czochralski process. These four Bridgman boules were equiaxed polycrystalline but appeared to be single-phase. The fifth Bridgman run was made with a charge made up from the "first to solidify" regions of the four Bridgman boules. This boule was columnar grain polycrystalline. This approach was not pursued further because of the termination of the program, but it did give promising results.

Chemical and Hall analyses showed the InP boules to be quite uniform in composition along their axes and to have approximately the same impurity levels as the raw material purchased from the Monsanto Co. Achieving the desired carrier concentration in single crystals will probably require higher-purity starting materials, since little segregation of impurities is apparent.

6. GaSb

Four GaSb growth experiments were made. The growth conditions are summarized in Table 10 and the results of chemical and Hall analyses are given in Table 11.

Severe problems were encountered with the formation of a non-volatile, solid film on the surface of the GaSb melts. Long soaks at temperatures above the GaSb melting point in N_2 or Ar-H_2 atmospheres and repeated remelting of etched charges were not effective in eliminating the oxide film. A B_2O_3 layer was used in runs 2a and 2b to dissolve the "oxide" from the surface of the melts. It was apparent that the surface of the melt began to clear in run 2a, which was held for 20 hours at 950°C. However, the viscosity of the B_2O_3 apparently increased with dissociation of the film and the clearing process stopped. The GaSb-2a charge was solidified in the crucible, re-etched and melted with a new B_2O_3 layer (GaSb-2b). This melt remained clean throughout

the crystal growth run and the B_2O_3 was sufficiently fluid that it did not interfere with the growth process. A single crystal having the same orientation as the seed was grown in this run.

Two GaSb crystals (GaSb-3 and -4) were grown from melts synthesized from mixed elements in vitreous carbon crucibles. The GaSb-3 melt was reacted and melted without a B_2O_3 encapsulant. A solid film formed on the melt surface and prevented single crystal growth, as had been the case with GaSb-1 and -2a. The charge was solidified, etched and remelted with a B_2O_3 encapsulant and the surface remained clean throughout the encapsulated crystal growth run. The GaSb-4 melt was made up from the remainder of the GaSb-3 charge and the GaSb-3 boule. The GaSb-3 boule was poorly shaped and contained one growth twin. This crystal was also grown from a B_2O_3 encapsulated melt to prevent the formation of a solid film on the surface of the melt.

The chemical and Hall analyses reported in Table 11 show that, like InP, the boules were uniform in composition and had approximately the same properties as the raw material. There is apparently little segregation of the impurity(s) responsible for the electron deficiency in GaSb. The impurities causing the observed p-type behavior have not been identified positively but Si may be partially responsible.

Silicon acts as a donor in GaSb[4] and is present both in the raw material (Monsanto) and the crystals at approximately the same levels, which agrees with the Hall measurements. No published data for the distribution coefficient of Si in GaSb was located; however, attempts to lower the impurity level by repeated zone refining have not been successful, suggesting a distribution coefficient near unity. If this is the case, lower carrier concentrations will be achieved only by using higher-purity starting materials.

7. InSb

The growth parameters used to produce characterized InSb boules are summarized in Table 12. The resulting chemical and Hall analyses are given in Table 13. Several growth runs were made with melts made up from mixed elements to establish growth parameters prior to using high-quality

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feed materials. Boule 1d was the fourth boule grown from the first melt. The results of other growth runs were not included because the boules were generally remelted prior to characterization.

The surfaces of melts made up from mixed elements were covered by solid films. Numerous attempts were made to eliminate it by etching solidified melts or pulling the solidified surface from the still-molten InSb. In every case the surface film reformed. In the fourth remelting of Melt 1, when boule 1d was grown, "oxidation" occurred at a greatly reduced rate indicating that the melt rather than the atmosphere was the source of the contaminant (oxygen).

It was observed during the InSb-1 and -2 growth experiments that if any oxide was present on the melt surface adjacent to the growth area, surface nucleation would produce a polycrystalline boule. This effect is demonstrated by boule 1d, which is a single crystal, and by boule 2, which is polycrystalline. The melt from which boule 1d was pulled remained essentially free of the oxide in the area adjacent to the growth interface throughout most of the run.

An InSb-3 was grown with material purchased from the Monsanto Co. This melt remained entirely free of the oxide throughout the entire run, which verified that control of the furnace atmosphere was satisfactory and that the oxide film observed during previous runs resulted from impurities in the feed materials.

The first three InSb growth runs were carried out in vitreous carbon crucibles (Vitreous Carbons, Ltd., England). The melts showed no tendency to wet or stick to crucibles. Only one crucible was broken as a result of the volumetric expansion which occurs upon solidification, and it had a layer of B_2O_3 over the InSb surface. There was some indication that molten antimony wets vitreous carbon, but it did not cause any problems during melting or growth.

All of the InSb boules were grown using a <111> seed purchased from the Monsanto Co. with the "A face" away from the melt. Boules grown from melts that were free of oxide (1d and 3) assumed the same orientation as the seed which was approximately 10° from a <111> axis.

Besides being 10° off the desired <111> axis, this InSb seed contained many striation boundaries. As a result, it was necessary to neck the single crystal to approximately a 2-mm diameter to produce crystals which were free of the substructure observed in the seeds. InSb crystals 1d and 3 had a higher crystallographic quality than the seed material.

The InSb-4 growth run was undertaken partly to determine whether InSb could be grown under vacuum. A solid surface film formed soon after the InSb melted in vacuum, and vaporization losses from the melt were obviously high from the rate of condensation on the cooled furnace walls. The solid surface film disappeared soon after the furnace was brought to atmospheric pressure. The InSb-4 boule was polycrystalline and has not been characterized further.

Hall samples were cut from both single-crystal boules. The results of these experiments at liquid nitrogen temperature are given in Table 13, along with the characteristics of the feed materials reported by Monsanto and our spectrographic analyses. The carrier concentration and mobility observed in crystal 1d are surprisingly good compared to values normally observed for III-V compounds that have been synthesized by the most elaborate procedures. Boule 3 has a carrier concentration approximately two orders of magnitude lower than that of boule 1d and is well within the program goal. The carrier concentration in boule 3 is the same order of magnitude reported by Monsanto and indicates that little contamination was introduced during crystal growth. The mobility is roughly an order of magnitude lower, which may be caused by crystallographic defects in the boule. Both boules are good single crystals.

VI. CONCLUSIONS

The liquid-encapsulation melt process has proven to offer a number of advantages for the growth and synthesis of III-V compound semiconductors compared to the techniques normally employed.

The process is particularly applicable to the growth of crystals from melts having high vapor pressures: the arsenides and phosphides. It has also proven useful for either dissolving the oxides from antimonide melts or upgrading the charges so a solid surface film does not form during the crystal growth process. The following are some specific advantages of the growth technique:

(a) Seeded Czochralski growth can be undertaken with substantially better visibility of the growth process than is usually attained with the hot-wall autoclave processes.

(b) The maximum diameters of crystals that can be grown by this process are limited only by the same factors which set upper limits in conventional Czochralski or Bridgman growth. Growth of arsenide and phosphide single crystals with diameters in excess of 3 inches appears entirely feasible.

(c) The stresses in the walls of the furnace system are confined to cooled areas. This substantially reduces the problems associated with preventing corrosion of the furnace and insuring the safety of personnel when the furnace is operated at the pressures and temperatures for the phosphides.

(d) The hot phosphorus and arsenic vapors are not generally present in the furnace chamber, which eliminates a major source of melt contamination. Also, the growth station materials can be freely selected to minimize contamination since they are not load bearing.

Compounds with highly volatile constituents can be synthesized under a liquid encapsulant. Stoichiometric GaAs melts as large as 120 gms, were synthesized under a B_2O_3 encapsulant. GaP melts

synthesized by the same technique were phosphorus-deficient, but the technique appears equally useful for it and other compounds. The GaAs crystals grown from melts that were synthesized by this technique indicate that high purities can be achieved. In fact, the technique appears to be especially attractive for GaP synthesis since contamination of the high-surface-area sponge would be avoided. The encapsulant remained clear after synthesis, permitting Czochralski, and of course Bridgman, growth to be initiated without handling the melt further.

The purity of the B_2O_3 used as the encapsulant is a major factor in producing high-quality crystals by this technique. Both metallic elements and dissolved and/or absorbed water-impurity levels must be carefully controlled. The material purchased from the British Drug House, Ltd., has been found sufficiently free of type II and IV elements to be useful. Drying and storage procedures have been developed which reduce the dissolved water to suitable levels. The boron contamination of the melts by the B_2O_3 encapsulant is surprisingly low, generally less than 1-10 ppm by weight.

The selection of a suitable crucible material is clearly more complex for high-temperature crystal growth with a liquid-encapsulated melt than when no encapsulant is used. The crucible must be able to contain both liquids for the duration of the growth run without contaminating the encapsulated melt. High-purity fused silica has proven as satisfactory for growth of high-purity III-V compound crystals in the presence of a B_2O_3 encapsulant as they have when no encapsulant is used. There is some evidence of contamination of the crystals by Si from the SiO_2 crucibles. Vitreous carbon has been used satisfactorily with GaSb, InSb, and InAs. Pyrolytic BN crucibles were used successfully with InP and GaAs encapsulated melts. The pyrolytic BN crucibles were the only ones which could be used more than once.

Single crystals of GaAs, GaP, and InSb were grown from commercially available raw materials which meet the carrier concentration goal of the program ($N \leq 10^{16}$ per cm^3). Negligible purification resulted during solidification of InAs, InP, or GaSb. At present, it appears that sources

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for higher-purity raw materials must become available if significantly higher-purity crystals of the latter materials are to be produced. GaSb raw material is particularly impure.

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APPENDIX A

SETUP AND SHUTDOWN PROCEDURES

SETUP PROCEDURE

(1) Remove the upper and lower shaft glands for cleaning and inspection. Replace O-rings and felt wipers as necessary. (They are normally replaced after each high-pressure, phosphide crystal growth run.)

(2) Lightly coat the upper and lower shafts with vacuum grease before placing them in the shaft glands. After the shafts are in place, remove the grease from the portion of the shafts inside the furnace with a wiper moistened in acetone.

(3) Replace the crystal growth station package (rf coil, heat shields, graphite susceptor, molybdenum support, discs, and spacers) and the inner infrared absorbing window.

(4) Position thermocouple within 1/8" of the maximum height. An ohmmeter is connected to the thermocouple to indicate when the junction contacts the protection tube or susceptor. The thermocouple is then withdrawn no more than 1/8".

(5) Connect the melt contact wire to the electrical feed-through and position the melt contact (high pressure furnace only).

(6) Insert the crucible and charge into the susceptor. Position the electrical contact in the crucible.

(7) Attach the seed-seedholder assembly to the upper shaft.

(8) Position the dried B_2O_3 in the crucible.

(9) Close the port.

(10) Open the gas inlet valves at the chamber to permit evacuation of these lines with the rest of the system. The valve at the gas regulator should be closed if the regulator cannot support a vacuum.

(11) Check the mechanical operation of the pulling shafts.

(12) Turn on the cooling water to the diffusion pump, induction coil, furnace chamber, and water-cooled seed shaft, if used.

(13) Evacuate the system to 10^{-5} torr.

TERMINATION OF THE GROWTH RUN

(1) Lower the furnace temperature and shut off rf generator.

(2) Lower ambient gas pressure to below 300 psig.

(3) Allow the system to cool to room temperature.

(4) Open the furnace and remove crystal. An air mask should be worn when the chamber is open after phosphide growth runs until the furnace has been cleaned thoroughly.

(5) Lower the thermocouple tip out of the furnace chamber by dropping the body of the thermocouple down through the lower pulling shaft.

(6) Remove the growth station package (rf coil, heat shields, graphite susceptor, molybdenum support, discs, and spacers) and the inner infrared absorbing window for cleaning.

(7) Recap the furnace coil flanges with blank plates, after removal of the rf coil, to prevent accidental flooding of the furnace system.

(8) Wipe the chamber walls with disposable wipers moistened in acetone to remove condensed arsenic and phosphorus. Polyethylene gloves and an air mask should be worn during cleaning. The wipers should be sealed in a plastic bag prior to disposal.

APPENDIX B

PREPARATION OF BORIC OXIDE (B_2O_3) ENCAPSULANT

(1) Put 15-20 grams of untreated B_2O_3 into the Pt-Au alloy crucible using polyethylene-covered tongs or polyethlene gloves.

(2) Load the crucible into the furnace.

(3) Pump the furnace down to approximately 5×10^{-4} torr.

(4) After turning on the water cooling to the resistance elements, follow the degassing heating cycle shown below.

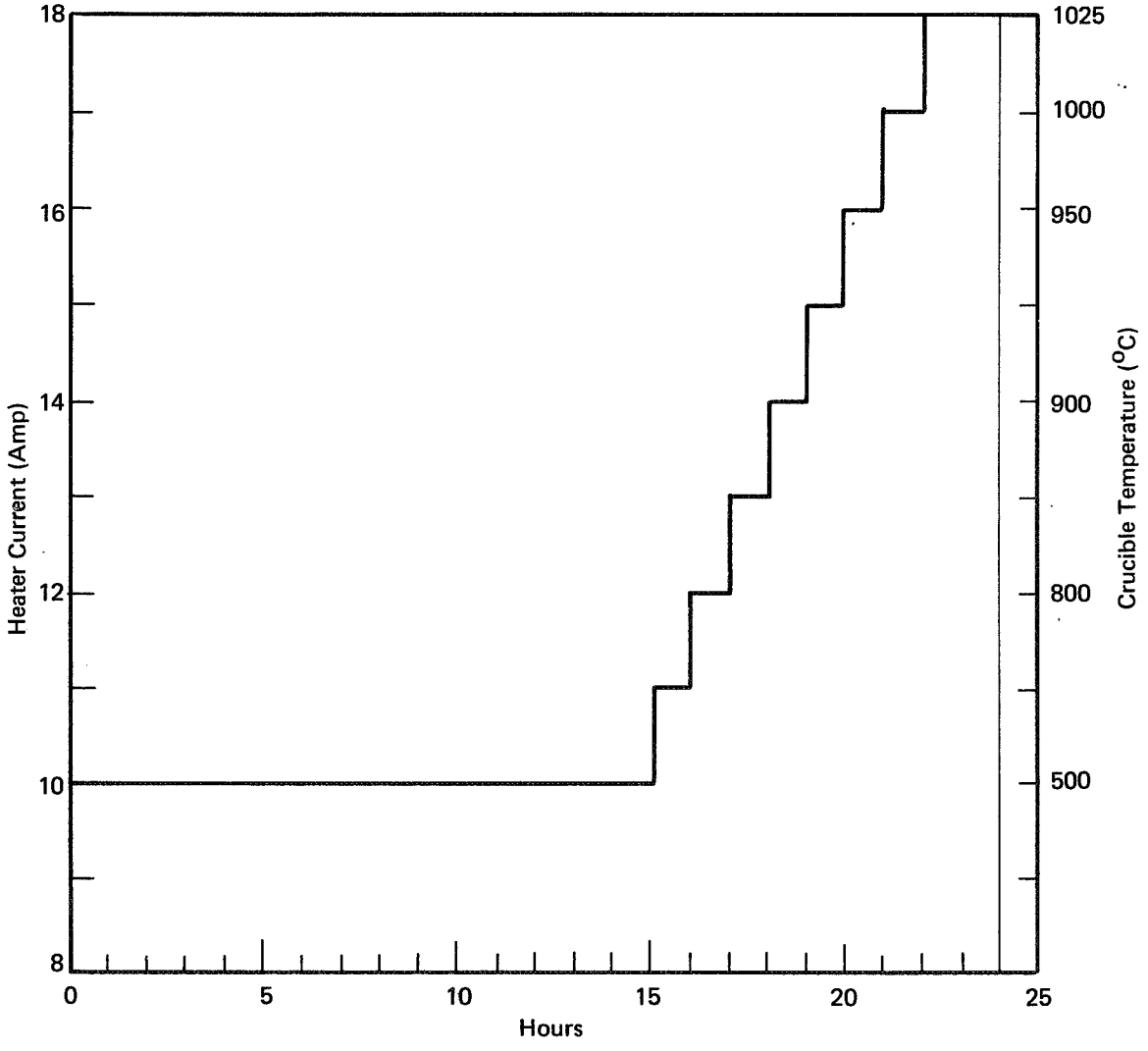


FIGURE B - 1 DEGASSING HEATING CYCLE

(5) After degassing and cooling to room temperature, place the charge in a vacuum desiccator. Handle the charge with disposable polyethylene gloves. The charge is stored at a pressure of 25 microns Hg.

APPENDIX C

MATERIALS HANDLING PROCEDURES

SAFETY

Wrap incoming arsenide and phosphide bulk materials in plastic, seal with tape, and store in a desiccator to avoid reaction with water vapor and other contaminants. In bulk form at room temperature these compounds do not present any hazard unless ingested. The porous GaP sponge should be stored in a dry atmosphere, since it will react spontaneously with water in warm, humid atmospheres.

Cut charges for melts from these bulk materials by sawing them under a water blanket in a hood. Small amounts of arsine (AsH_3) or phosphine (PH_3) gases may be generated during the cutting operation but should be contained within the hood. Fine particulate debris resulting from the cut should be continuously flushed into the drain as it is generated. Keep the wire saw and the surrounding area in the hood clean, and wear either rubber or polyethylene gloves when cutting or polishing these materials.

All of these materials must be acid-etched before they are placed in crucibles for crystal growth runs. As several toxic gases can be generated during these reactions, all etching should be done in hoods by personnel wearing polyethylene gloves.

Crystal growth is carried out in closed furnace systems containing nitrogen, argon, or argon-hydrogen atmospheres. Establish the ambient furnace atmosphere after evacuation to high vacuum. (All vacuum pumps should exhaust directly into hood ducting.) Ambient gas pressures range from 1 to 55 atmospheres. Discharge lines from the pressure relief safety valves should be connected to hood ducting.

Arsenic and phosphorus vapors from GaAs, InAs, GaP, and InP melts will condense on the cold furnace walls. Upon exposure to air after the

furnace is opened, they can react with water vapor to form arsine and phosphine. Therefore, before opening the furnace, flush the cooled system with nitrogen or argon gas to remove the arsine and phosphine generated during crystal growth. A small hood connected to flexible ducting should then be positioned directly above the furnace access port to collect any remaining gases and any arsenic or phosphorus dust that may remain.

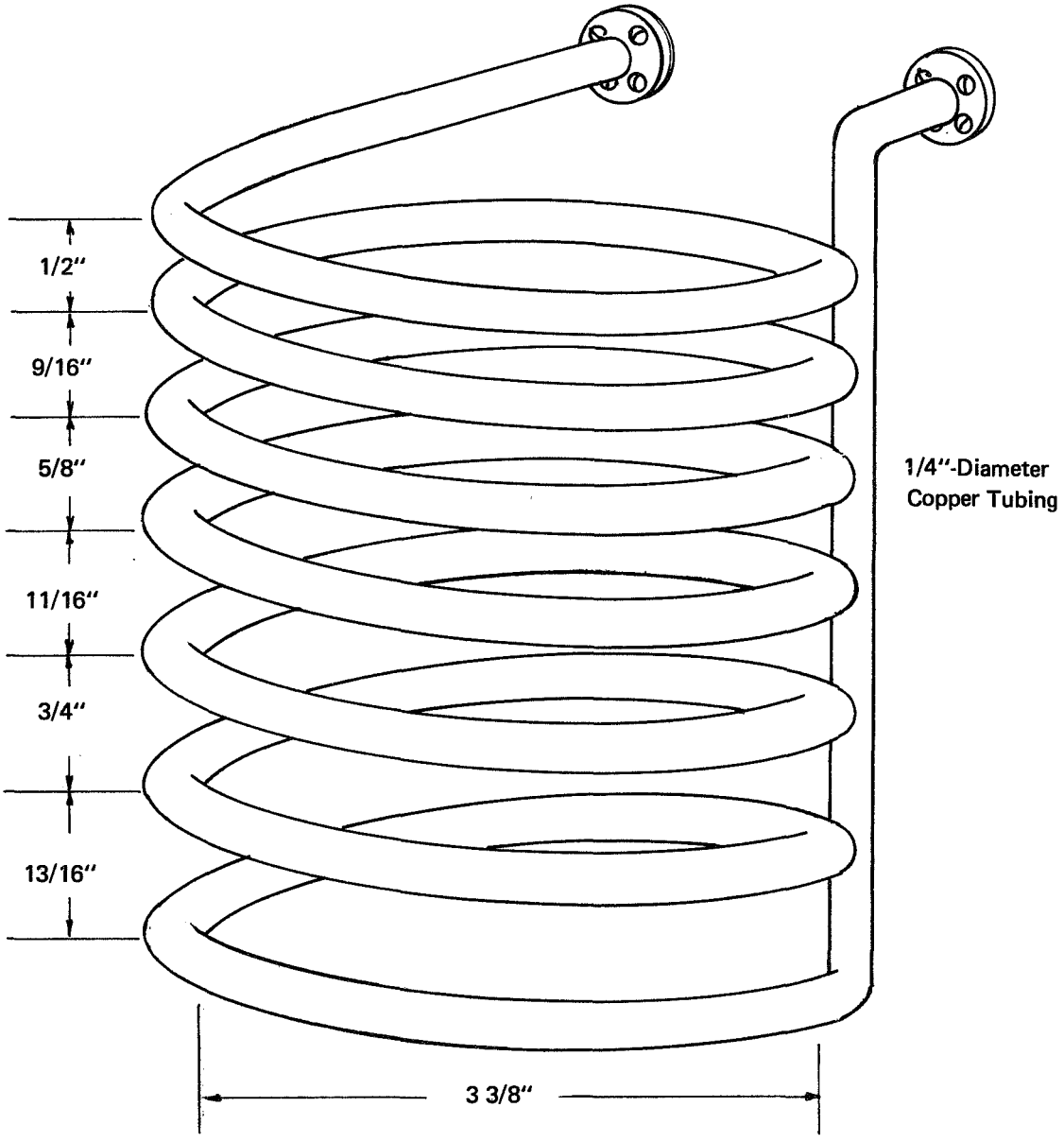
Using paper towels, wipe off the arsenic or phosphorus that condensed on the furnace walls during the crystal growth run. Use high-purity acetone, alcohol, or freon as a solvent for the final cleaning steps. Always wear gloves when cleaning. Store the paper towels, which contain powdered arsenic or phosphorus, in sealed plastic bags; this will prevent the powder from escaping into the room or reacting with water vapor to form arsine or phosphine. Be sure that these bags are safely disposed of.

Place compressed air tanks and breathing masks adjacent to the furnace so that they will be readily available if needed.

CHEMICAL POLISHING

The following solutions have been found satisfactory for chemical polishing at room temperature:

GaAs	60%	HNO_3
	20%	HF
	20%	H_3PO_4
InAs	60%	HNO_3
	20%	HF
	20%	H_3PO_4
GaP	50%	HNO_3
	50%	HCl
InP	96%	HCl
	4%	HNO_3
GaSb	50%	HNO_3
	25%	HF
	25%	Glacial Acetic Acid
InSb	50%	HNO_3
	25%	HF
	25%	Glacial Acetic Acid



APPENDIX D rf COIL CONFIGURATION