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FIRST QUARTERLY TECHNICAL REPORT

Report Date: April 14, 1963

December 14, 1962 to March 14, 1963

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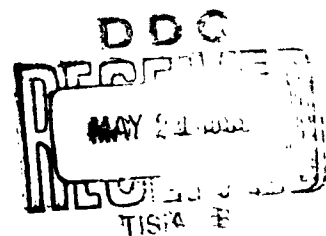
"GALLIUM PHOSPHIDE DEVICES"

CONTRACT NR. DA-36-039-AMC-00103 (E)

Placed By:

U. S. Army Electronics Material Agency

Fort Monmouth, New Jersey



THE EAGLE-PICHER COMPANY

Chemicals & Metals Division,

Research Laboratories,

Miami, Oklahoma

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"GALLIUM PHOSPHIDE DEVICES"

Order Number 5358-PM-63-91

Date of Contract: December 13, 1962

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Fort Monmouth, New Jersey.

I. PURPOSE

The purpose of this investigation is the growth of single crystal gallium phosphide suitable for device applications; the evaluation of such material; and the fabrication of devices.

The material category encompasses the selection of a suitable method of synthesis; growth of single crystal material of best purity, and refinements in techniques aimed at producing the largest single crystals practicable, of highest possible purity.

The Evaluation program is to include initially the analysis or measurement of impurity concentrations; the resistivity, mobility and lifetimes. Subsequently, in the device fabrication stage, evaluation is to include the determination of doping techniques, doping efficiencies of the common donor and acceptor elements, and relating such factors at least generally to resistivity, mobility and device parameters.

The fabrication program is aimed primarily at single junction devices, of rectifier nature, although three terminal devices are contemplated as a logical extension as an aid in full evaluation of the junction parameters. Evaluation of the two and/or three terminal devices is to include diode rectifying properties, contact ohmicity, temperature performance at elevated temperatures, junction luminescence effects, and any further parameters considered important and relevant in the opinion of the Government Contracting Officers Representative.

II. ABSTRACT

Synthesis of Gallium Phosphide by an open flow technique, by passing Phosphorus vapor over gallium sesquioxide in a hydrogen atmosphere was accomplished. Variations in color, texture, and unreacted components were noted. Studies involving varying temperatures, flow rates and time were carried out for the purpose of rationalizing product differences. Synthesis was best when phosphorus temperature and flow rate were low; and when the Ga_2O_3 charge had minimum temperature gradients across it.

An alternate synthesis process was tried, involving phosphorus trichloride vapor passed over elemental gallium heated and stirred by induction heating. Results were poor and appeared non-productive.

Melt growth of the synthesized material was carried out. A total of 15 melts were made. Several were aborted due to malfunctions in furnacing. Several were partially successful, but produced heavily occluded ingots. Several were successful in that ingots were clear, with few if any inclusions and good crystal structure, although not single crystal. Ingots were from 3 to 7 grams in weight. Samples of several of these were delivered to Mr. Robert Yatsko at Fort Monmouth, New Jersey on February 13, 1963.

Vapor phase growth studies were done in parallel with melt growth. Initial results appear promising. Several seed plates were grown having crystallites up to 5 mm per side. Crystal structure was excellent as determined by Laue X-ray analysis.

Initial exploration of polishing, cleaning and etching techniques have been carried out. Methyl alcohol saturated with chlorine gas is found effective as an etchant and polishing solution.

Preliminary efforts on contacting GaP has indicated alloyed indium-gold to be an acceptable high temperature contact.

III. PUBLICATIONS, CONFERENCES AND REPORTS

Reports:

Monthly Letter Report No. 1 was prepared and delivered on January 16, 1963.

Monthly Letter Report No. 2 was prepared and delivered March 13, 1963.

Conferences:

A conference was held at Fort Monmouth, New Jersey on February 13, 1963. Present were Messrs. Robert Yatsko, Phillip Newman and James Kesperis. The subject of the conference was current progress of the investigation, projected guide lines for fabrication and evaluation of materials and devices, and inspection of GaP material samples. The following samples were delivered to Mr. Yatsko.

M6302AV GaP Slice from Ingot M-5

M6302AW GaP Slice from Ingot M-8

M6302AX GaP Slice from Ingot M-9

IV. FACTUAL DATA

Introduction

The investigation of gallium phosphide devices is divided into four major categories, i.e., materials, material evaluation, device fabrication and device evaluation. Figure 1 graphically illustrates the chronological planning of these phases. It is understood that this planning is tentative due to the unpredictable nature of any research program.

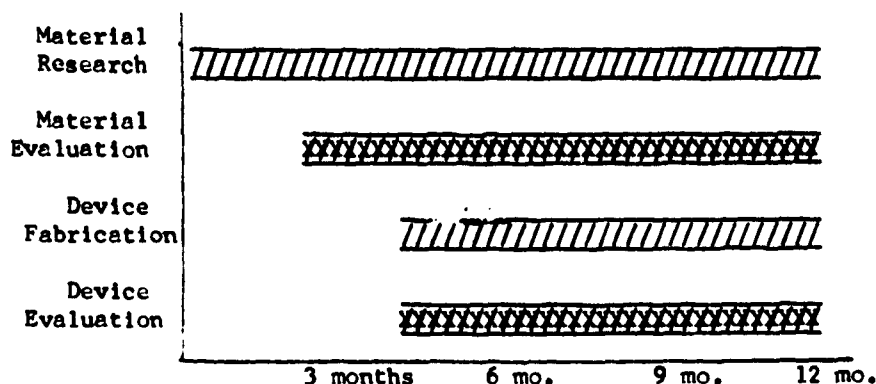


Figure 1. Chronology of Phases of Investigation.

The initial phase of material research was begun promptly and effectively. It was proposed that a two step technique be used to prepare device quality GaP. Synthesis by an open flow technique and melt growth of crystals under pressure was selected as the most practical and feasible method of obtaining the material without a lengthy materials investigation. The synthesis program has produced material suitable for melting. The uniformity and reproducibility of the technique has been acceptable but can be improved.

Studies of the effect of temperatures, flow rates, etc. have been carried out in the production runs and have noticeably improved uniformity and reproducibility. Recovery rates have been from 50% to 75% and appear

amenable to further increase. Initial high impurity levels were traced to phosphorus impurities, and have been significantly decreased. Attempts to scale up the synthesis in volume have been handicapped by the complementary introduction of larger furnace temperature gradients. Progress is expected in this area also. Brief investigation of alternate synthesis techniques have been explored when judged feasible. One such technique, considered and explored briefly, involved phosphorus trichloride vapor carried by helium gas over elemental gallium, heated to 1150°C. by induction heating. It was considered that the synthesized GaP would be taken into solution in the gallium, aided by the stirring effect of induction, and precipitate at the cooler end of the gallium as a crystal. The results of a 10 hour run indicated synthesis did occur, but growth was so slow it did not appear practical. An alternate system is under consideration now but is not a part of this report.

Melt growth studies have been carried out to improve size and crystal uniformity. In general, melt-growth has been successful and appears practical. The technique involves melting the synthesized material, in fused quartz ampoules, with an internal pressure of phosphorus vapor approximately equal to the decomposition pressure (approximately 30 atmospheres). A slightly greater external-to-the-ampoule pressure of argon gas is maintained in the furnace during the melt cycle. Approximately ten of the melt runs produced GaP ingots, transparent or translucent, with inclusions varying from none to several per ingot. Four or five suffered significant decomposition or were otherwise unusable due to rupture of the ampoules or furnacing difficulties.

Several experimental melt-runs were made using various ampoule shields (tungsten carbide, silicon carbide, graphite, etc.) to establish

melt temperatures, holding time, etc. These resulted in sintered or partially melted charges.

Both Laue and Debye Scherrer X-ray analyses were used to define the structure and stoichiometry of the ingots. Results in every case indicate very good crystal structure, and unit cell dimensions uniformly agree with published data on GaP. Detailed analysis is made subsequently of these data.

Spectrographic analysis indicates acceptably low impurity levels. The major impurity is silicon, which is due to the quartz environment in both synthesis and melt growth. Some indications were observed that the silicon content was significantly increased when unreacted gallium oxide exists in the charge. This observation, while tentative, offers promise of holding the silicon contamination to minimal levels.

Vapor phase transport has been explored in parallel with melt growth. This was undertaken based on the long background and experience of this laboratory in vapor phase growth of large II-VI crystals. Results to date are promising. Seed plates of optically flat quartz are used and have produced plates of GaP up to one inch in diameter. Thickness has been limited by the limitations, self imposed, on volume of charges. Nevertheless, fairly large single crystallites up to 5 mm on a side have been observed. Detailed discussion of this work is included in this report. The technique is attractive, and is considered worthy of further parallel study.

Material evaluation is as yet incomplete. Evaluation thus far has been principally concerned with crystal structure and impurity analysis by emission spectroscopy. As previously mentioned the crystal structure

is good, with little evidence of strains, etc. Impurity content still leaves room for improvement, but is acceptably low for this stage of the investigation. Thermal typing indicates "n" type material, with donor concentrations rather low. Subsequent study is to be made of doping, during synthesis, growth, or both.

Device fabrication is in the early stages as yet. Contacting by alloy methods has been accomplished. Alloy junction fabrication is currently in progress. These data are not considered complete or firm enough to warrant inclusion in this report.

Gallium Phosphide Synthesis*

Gallium phosphide is synthesized by an open flow technique to be described in detail subsequently. The synthesis of gallium sesquioxide with elemental phosphorus vapor is carried out in a hydrogen atmosphere.

The gallium sesquioxide used in the gallium phosphide synthesis was obtained from The Eagle-Picher Company.

Impurity analyses of the oxide were determined by emission spectroscopy and results are given in Table I. The Ga_2O_3 is much the purest of the components used. Any contribution of the oxide to final impurity levels is hidden by those contained in the phosphorus or picked up in processing.

* The work on this phase was performed by S. Roderique.

TABLE I

SPECTROGRAPHIC DATA - GALLIUM SESQUIOXIDE

<u>Eagle-Picher Lot No.</u>	<u>Impurities in ppm.</u>				<u>Total Impurities</u>
	<u>Cu</u>	<u>Si</u>	<u>Ca</u>	<u>Mg</u>	
137-1	.34	<.10	.660	.150	1.150
A-141 Tray #16	.23	.65	.039	.082	1.001
A-141 Tray #18	.15	.43	.052	.140	0.772

Elemental Phosphorus

Elemental phosphorus used for synthesis of gallium phosphide was obtained from two sources: (1) Fisher special micro grade, and (2) American Agricultural Chemical Company semiconductor grade.

Both sources initially indicated a high level of impurities; however, selection by batch lots as indicated in Table II, provided high purity material.

The American Agricultural Chemical Company's semiconductor grade was found to be superior to the Fisher micro grade. Therefore, the better material was used in subsequent runs.

TABLE II

SPECTROGRAPHIC DATA PHOSPHORUS IMPURITIES

American Agricultural Chemical Company
Phosphorus

Reference Number	Lot No.	Impurities in ppm.						
		Si	Sn	Mg	Fe	Al	Cu	Ca
M6301CB	Q-002	40.0	5.0	4.0	1.0	5.0	2.0	10.0
M6302AA	Q-003	ND	ND	ND	ND	ND	0.5	ND
M6301CB	Q-004	ND	ND	ND	ND	ND	ND	ND
M6303DC	Q-005	20.0	ND	2.0	.5	5.0	1.0	10.0
M6303BX	Q-006	20.0	ND	2.0	.5	5.0	0.5	6.0

Fisher Special Micro Grade

Reference Number	Impurities in ppm						
	As	B	Mn	Mg	Pb	Sn	Si
M6212BV	50.0	5.0	5.0	50.0	50.0	1.0	5000.0

Reference Number	Impurities in ppm						
	Ga	Fe	Al	Cu	Ti	Ca	Cr
M6212BV	5.0	500.0	500.0	50.0	50.0	5000.0	5.0

Note: "ND" = None Detected.

In order to determine if the phosphorus was purified to any degree through the sublimation process during synthesis, the following comparison was carried out. A 10% heel was left in the boat and the impurities in this heel were compared with that of the original phosphorus by spectrographic analyses. The data are given in Table III; they indicate that significant purification does occur during the sublimation. It appears feasible to obtain a product with lower impurities than the starting phosphorus levels. However, this does not imply that none of the phosphorus impurities carry over.

TABLE III
SPECTROGRAPHIC DATA ON PHOSPHORUS BEFORE AND AFTER SUBLIMATION

Reference Number	Run Number	Phosphorus Lot Number	Impurity Analyses	
			Total ppm Before Sublimation	Total ppm Heel After Sublimation
M6212BV	OF-8	Fisher	7×10^3	2×10^5
M6301CC	OF-9	A*CC Q-004	ND	6.0
M6301CO	OF-11	" Q-004	ND	6.0
M6302AE	OF-13	" Q-003	.5	10.5
M6302AS	OF-15	" Q-003	.5	100.0

Note: "ND" = None Detected.

Synthesis

The technique used to synthesize GaP is best explained by referring to Figure 2, which illustrates schematically the system. A fused quartz tube 35 mm in diameter (5) is housed in a three zone furnace (6). A charge of dry Ga_2O_3 (8) is placed in a boat in one end zone; a charge of high purity phosphorus in a small boat (7) is placed in the other, upstream end zone. The system is sealed up and high purity argon (1) used to purge the system, through a dry-ice/acetone trap (3) and molecular sieve towers (4). Gas exits through a dry ice condenser (9), bubbler (10) and is exhausted to the atmosphere. When purging is complete, hydrogen gas is introduced and the flow maintained long enough to insure displacement of the argon. Hydrogen flow rate is then adjusted and the furnace energized. Temperature of the Ga_2O_3 is raised rapidly to 1000°C , simultaneously the phosphorus zone is raised to 400°C . Center zone temperature is adjusted to 700°C . The prescribed temperatures are maintained until approximately 90% of the phosphorus charge is depleted, then the furnace is turned off. Hydrogen flow is maintained until cooling is complete; argon is used to purge the system.

During Synthesis the unreacted phosphorus is collected in the dry-ice condenser. The collected solids contain some white phosphorus which ignites if exposed to air. The containing tube (5) is taken apart immediately ahead of the condenser (9) and immediately stoppered. The condenser section is removed to a safe area and allowed to ignite and burn off. Phosphorus boat and synthesis boat are then safely and easily removed.

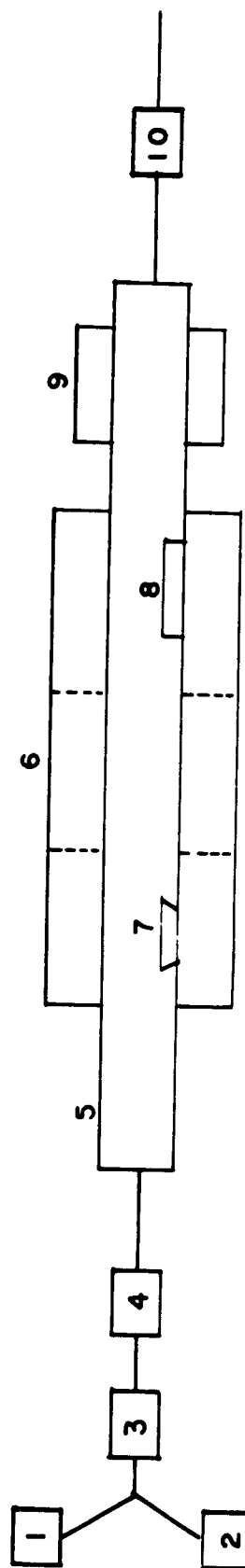


Figure 2. Open-Flow Gallium Phosphide Synthesis System.

1. Argon
2. Hydrogen
3. Acetone - Dry Ice Trap
4. Molecular Sieves
5. Quartz Tube
6. 3-Zone Furnace
7. Phosphorus Charge
8. Ga_2O_3 Charge
9. Dry Ice Condenser
10. Bubbler

The furnace used is a Hevi-Duty multi stage type having three separately controlled heat zones, as shown in Figure 3.

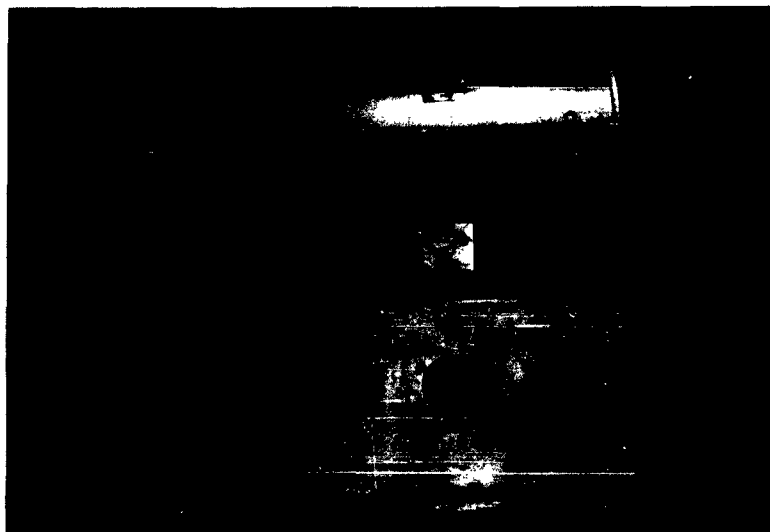


Figure 3. Hevi-Duty Three Zone Furnace

A study was undertaken to establish the optimums of phosphorus temperature, temperature of the gallium oxide, hydrogen flow rate, amount of excess phosphorus and duration of synthesis runs.

The gallium phosphide product varied in color and texture. The upper surface (usually needle growth) ranged from bright orange to yellow. On occasion the downstream end of the boat had trace amounts of white filamentary growth. This appeared to be sublimed gallium sesquioxide which had not been reacted. Where partial reaction occurred this growth had a yellow color. These two conditions were related to use of a long (about 7 inches) boat, where a temperature gradient was present along the

length of the boat. Where shorter boats (about 4 - 5 inches) were used the color was a more uniform orange.

Needle growth up to 1 mm diameter, was usually found at the downstream end of the boat, and frequently over the length of the boat. The degree of needle growth appears to be related to the temperature gradient along the length of the boat and hydrogen flow rates.

There were twenty two synthesis runs made during this work period. Twenty of these runs were made using the apparatus shown in Figure 2.

Table IV shows the synthesis data on several runs and points out some progressive changes that were made and results of same.

TABLE IV

GALLIUM PHOSPHIDE SYNTHESIS DATA

Run Number	Gallium Oxide Used Grams	Phos. Used Grams	Phos. Temp. °C.	Gallium Oxide Temp. °C.	H ₂ Flow L.P.M.	Duration Hours	Remarks
OF-5	14.1	6.9	450	1000	.3	3½	Unreacted Ga ₂ O ₃ at each end of boat. Orange needles on downstream surface.
OF-6	15.0	7.3	405	1010	.3	6½	Fine needles at upflow end of boat. Coarser needles at downflow end of boat.
OF-9	15.0	8.0	400	1000	.3	10	Heavy needles at downflow end of boat. Good conversion.
OF-12	15.0	9.0	415	1020	.8	6	Needles at downstream end of boat. Free Ga ₂ O ₃ present.
OF-13	15.0	9.0	400	1000	1.2	6	Needles at downflow end of boat. Conversion appeared to be complete.
OF-15	15.0	9.0	400	1000	1.2	7	Needles over all of top surface. Conversion appeared to be complete.

The conditions that have become standard procedure are given in run OF-15, with the exception of the length of the gallium oxide boat. Shortening the length of the boat reduces the temperature gradient along the boat. A further change contemplated involves use of two of the zones for the Ga_2O_3 to obtain essentially constant temperature of the entire charge.

To ascertain if it were feasible to rerun the synthesized material which contained unreacted gallium oxide, a run was carried out on this type of material.

Forty seven grams of material from runs OF-5, 6, 7 and 8 were placed in the gallium oxide boat and nine grams of phosphorus in the phosphorus boat. The run was then carried out as usual.

This run was a partial success. The material was more uniform in texture, and reddish orange in color. The unreacted component was diminished in quantity but, some was still present in the lower portion of the charge. A major portion of the product was reclaimed for use.

It appeared attractive to stir or agitate the gallium oxide during synthesis, therefore, an assembly was designed as shown in Figure 4. The segment of quartz tube containing the gallium oxide and phosphorus was arranged to allow rotation intermittently during synthesis.

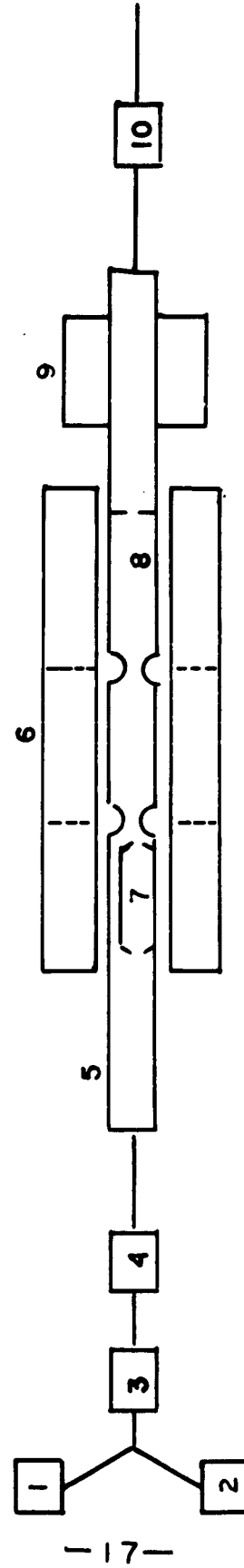


Figure 4. Open-Flow Gallium Phosphide Synthesis System.

1. Argon
2. Hydrogen
3. Acetone - Dry Ice Trap
4. Molecular Sieve
5. Quartz Tube
6. 3-Zone Furnace
7. Phosphorus Charge
8. Ge_2O_3 Charge
9. Dry Ice Condenser
10. Bubblor

. This method worked very well on a ten gram sample but, when the apparatus was enlarged to accommodate a fifty gram charge the results were not satisfactory. Several difficulties which became apparent were: (1) the gallium oxide had a tendency to sinter and cling to the inner surface of the tube in globules, (2) it gave poor conversion, (3) the tube had to be cut apart at the gallium phosphide section, and (4) the gallium phosphide was difficult to remove without contamination.

It was decided to revert to the former method of using boats and to concentrate our efforts on improving that method.

Spectrographic impurity analyses were made on various products of runs OF-5 through OF-22 and these data are recorded in Table V.

The data on run OF-5 show that the needles formed on the surface of the synthesized gallium phosphide are purer than the remaining gallium phosphide. Run OF-8 which is the most impure was made with Fisher micro grade phosphorus.

In run OF-11 it is indicated that the gallium phosphide found adjacent to the boat is lower in silicon impurity than the general product. This appears difficult to explain and directly contrary to expectations. Speculation on this anomaly seems useless until further data are obtained; in either case the silicon levels were not excessively high.

It will be noted that runs OF-15, 18, 19, 20, 21 and 22 are very consistent and lower in total impurity content. This improvement in purity and uniformity is a reflection of higher purity phosphorus, improved control of phosphorus sublimation during synthesis and refinements in the general synthesis technique.

TABLE V

SPECTROGRAPHIC DATA - SYNTHESIZED GALLIUM PHOSPHIDE

Reference Number	Number	Description	Impurities in ppm					
			Si	Mg	Fe	Al	Cu	Ca
M5212CG	OF-5	Needles on surface	10.0	3.0	2.0	ND	1.0	50.0
M6212CH	OF-5	Yellow crystals	30.0	30.0	10.0	20.0	3.0	50.0
M6212CI	OF-5	General Product	30.0	5.0	2.0	5.0	1.0	10.0
M6301AB	OF-6	Upstream end of boat	50.0	5.0	1.0	ND	2.0	20.0
M6301AC	OF-6	Downstream end of boat	50.0	5.0	1.0	ND	2.0	20.0
M6301AD	OF-6	White Material on surface	50.0	3.0	1.0	ND	3.0	20.0
M6301BM	OF-8	General Product	500.0	3.0	1.0	5.0	1.0	20.0
M6301CD	OF-9	General Product	10.0	2.0	ND	5.0	ND	10.0
M6301CL	OF-10	General Product	80.0	1.0	ND	ND	0.5	8.0
M6301CM	OF-11	General Product	40.0	3.0	5.0	15.0	1.0	20.0
M6310CN	OF-11	Adjacent to quartz boat	10.0	5.0	3.0	10.0	1.0	20.0
M6302AB	OF-12	General Product	50.0	3.0	2.0	5.0	2.0	10.0
M6302AD	OF-13	General Product	200.0	3.0	1.0	2.0	1.0	10.0
M6302AR	OF-15	General Product	7.0	3.0	ND	2.0	ND	ND
M6303BZ	OF-18	General Product	10.0	5.0	ND	ND	.5	10.0
M6303BY	OF-19	General Product	7.0	3.0	ND	ND	.5	5.0
M6303CP	OF-20	General Product	10.0	5.0	ND	ND	.5	10.0
M6303DA	OF-21	General Product	10.0	5.0	ND	ND	1.0	20.0
M6303DB	OF-22	General Product	7.0	3.0	ND	ND	1.0	10.0

Note: "ND" = None Detected

An alternate method of synthesis was explored. This process involved passing phosphorus trichloride as a vapor over elemental gallium using helium as a carrier gas. The gallium was heated by induction to 1150°C at one end. It was considered feasible that gallium phosphide, synthesized at the hot end, might diffuse as a solute in the gallium and grow as a crystal at the cooler end of the melt. Some synthesis did occur but formed as a deposit on the gallium and the tube walls. The method appears very slow and difficult to control. Further efforts have been suspended.

Although process efficiency per se is not considered a prime consideration, some analysis of recovery percentage is of interest. It has proved desirable to use excess phosphorus to insure full conversion and to minimize impurity transfer from the phosphorus to the Ga_2O_3 . Thus the recovery is calculated on the gallium content of the original Ga_2O_3 versus the gallium content of the GaP product. Considerable GaP product deposits on the wall of the tube and downstream from the charge. No allowance is made for this loss; nor is it reclaimed because of purity considerations. Thus the recovery percentages listed in Table VI are somewhat conservative. It is interesting that the recovery can be greater than 80%. It is considered that further refinement may evolve process parameters resulting in uniform high recovery values.

In summary, the open flow technique of synthesis appears practical, and amenable to control and improvement. This method has produced material suitable for melting. Reproducibility is good, and appears capable of further improvement. Purity levels are acceptable, and improving. Alternate techniques are being explored when feasible and may be productive.

TABLE VI

GaP RECOVERY RATES CALCULATED ON GALLIUM CONTENT

Run No.		Ga ₂ O ₃ Grams	Phos. Grams	Ga ₂ O ₃ Temp. °C	Phos. Temp. °C	Hydrogen Flow LPM	Duration of Run Hours	Recovery Ga ₂ O ₃ Per cent
13.02	OF-6	15.0	7.3	1010	405	.3	6½	81.1
7.3	OF-12	15.0	9.00	1015	415	.8	6	45.5
	OF-13	15.0	9.0	1000	400	1.25	5 3/4	51.8
9.0	OF-16	15.0	9.0	1000	410	1.25	9½	56.1
9.0	OF-17	15.0	9.0	1000	400	1.25	13	56.1
19.3	OF-20	25.0	15.0	1000	420	1.25	12	72.1
14.9	OF-22	20.0	12.0	1000	400	1.25	5	69.5

GROWING CRYSTALS FROM MELT*

GaP has a dissociation pressure in excess of 20 atmospheres at its melting point (1500°C). Melting of the GaP in fused quartz ampoules was desired to minimize contamination. Since quartz is semi-plastic at this temperature it was desirable to use a high pressure furnace to effectively equalize internal and external pressures on the ampoules. Phosphorus is included in the ampoule to provide a partial pressure of the order of 10 atmospheres.

The furnace (See Figure 5) is an internally insulated water cooled container with a lowering mechanism in the bottom. It is heated by a graphite element fed from a high current A-C source.

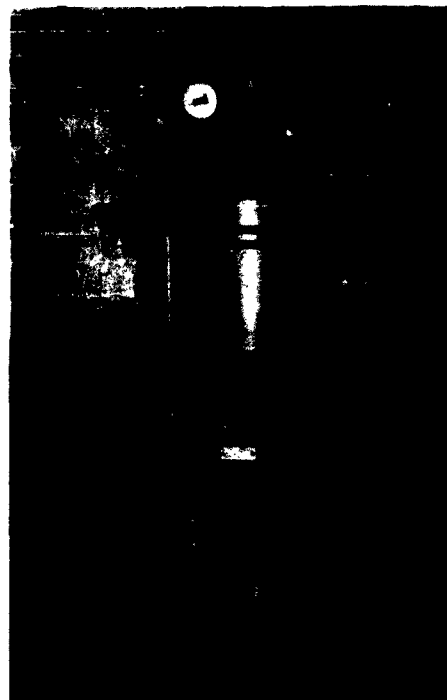
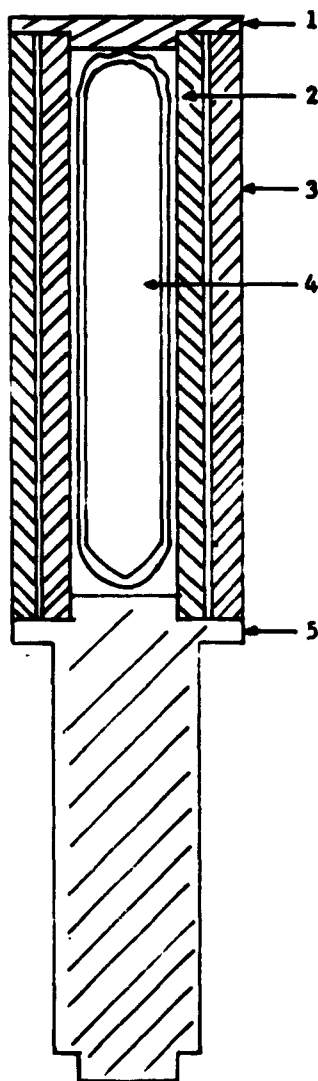


Figure 5
High Pressure, High
Temperature Furnace

* The work on this phase was performed by L. Brown.

Temperature control is accomplished by varying the A-C input to the heater. Use of the high pressure furnace required the design of a suitable crucible (See Figure 6).

The crucible includes the evacuated quartz ampoule (1) containing the charge and a graphite sleeve (2) of suitable dimensions to absorb any expansion of the ampoule. Around the graphite sleeve is a tungsten-carbide shield (3) to contain the interior components in event of higher stress. These pieces then sit on a graphite pedestal (4) of sufficient length to fit on the movable shaft of the high pressure furnace, which is withdrawn to accomplish the Bridgman crystal growing action. It allows a pulling distance of 1 1/4 inch. The top is then fitted with a graphite cap (5). This crucible is then fitted into the high pressure furnace as shown in the schematic diagram (Figure 7).



1. Graphite Top
2. Graphite Sleeve (16 mm I.D.
24 mm O.D.)
3. Tungsten-Carbide Sleeve,
(25 mm I.D. 36 mm O.D. 88 mm L)
4. Quartz Ampoule - 12 mm I.D.
15 mm O.D.
5. Graphite Pedestal - 60 mm L.

Figure 6. High Pressure Crucible for Melting GaP.

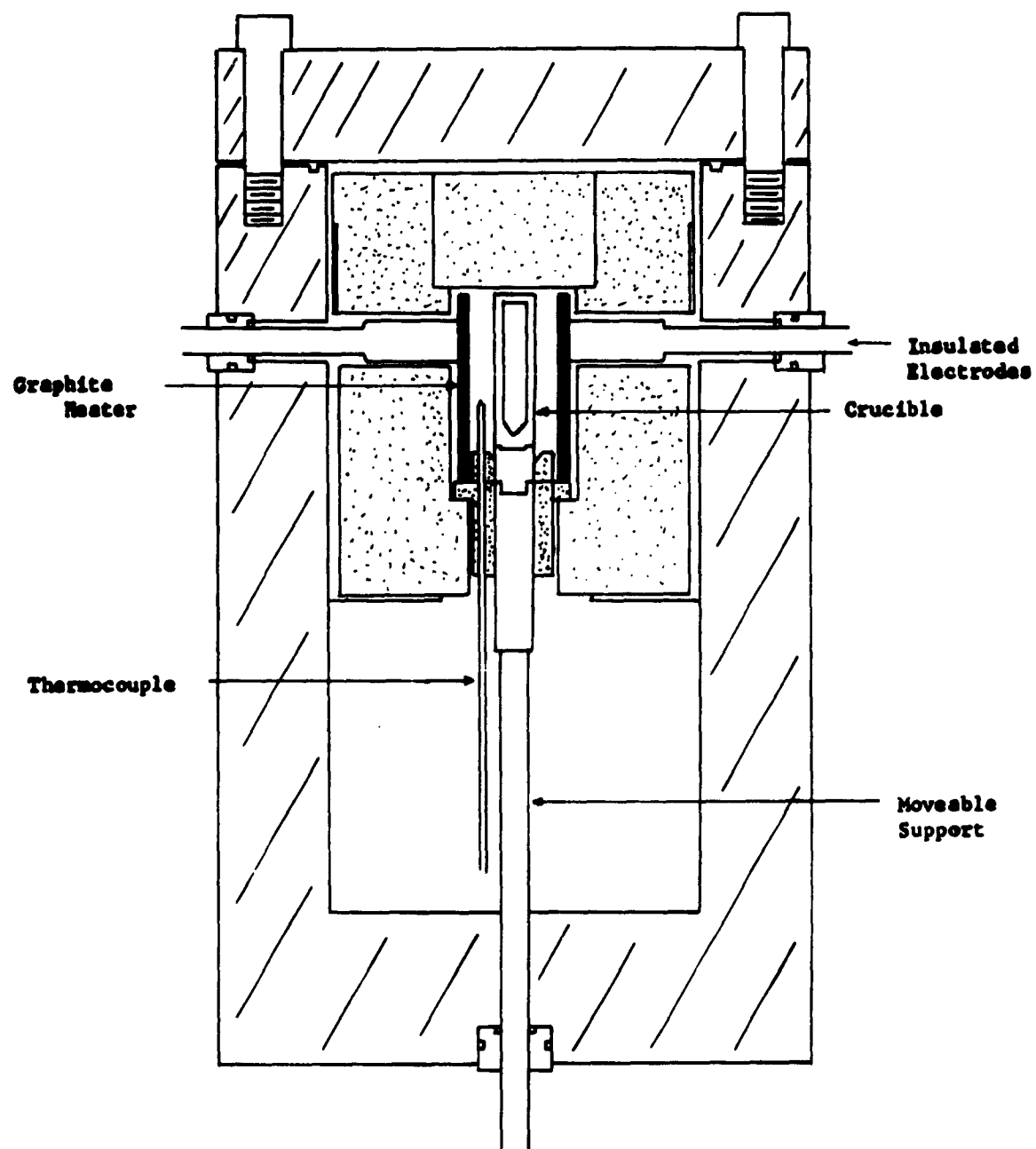


Figure 7. Schematic of High Pressure Furnace.

The furnace is then closed and sealed. It is purged by vacuum pumping and flushed with argon to reduce the residual oxygen content of the chamber for the protection of the graphite heating element. The argon pressure is then raised to the desired level. The furnace and recorder are switched on and the temperature is raised quickly to a predetermined level. The desired temperature is maintained for a sufficient time to allow stabilization and complete melting. After this period the withdrawal mechanism is set in operation at a selected rate and allowed to travel the predetermined distance. After the pull is completed the power is slowly decreased until the temperature is below the melting point of the GaP and then rapidly decreased. After sufficient cooling time the pressure is slowly reduced.

The temperature sensing system consists of a graphite-graphite thermocouple connected to a recorder. It incorporates a variable opposing voltage to expand the scale of the chart in segments of temperature. This opposing voltage is ordinarily set in one of 10 equal increments. This recorder was initially calibrated by the successive melting of different materials of known melting point. The temperature sensing system is one of the principal factors limiting reproducibility because of change in output with use. It has been concluded after many melt runs and by utilization of previous experience that the melting point of GaP is approximately 1500°C with a dissociation pressure of approximately 30 atmospheres. This is in reasonably close agreement with the unpublished work of D. Richman, R.C.A. Labs., Princeton, New Jersey⁽²⁾. Shown in Figure 8 is Richman's graph of the disassociation pressure of GaP transposed to temperature in degrees centigrade and lbs./sq.in.

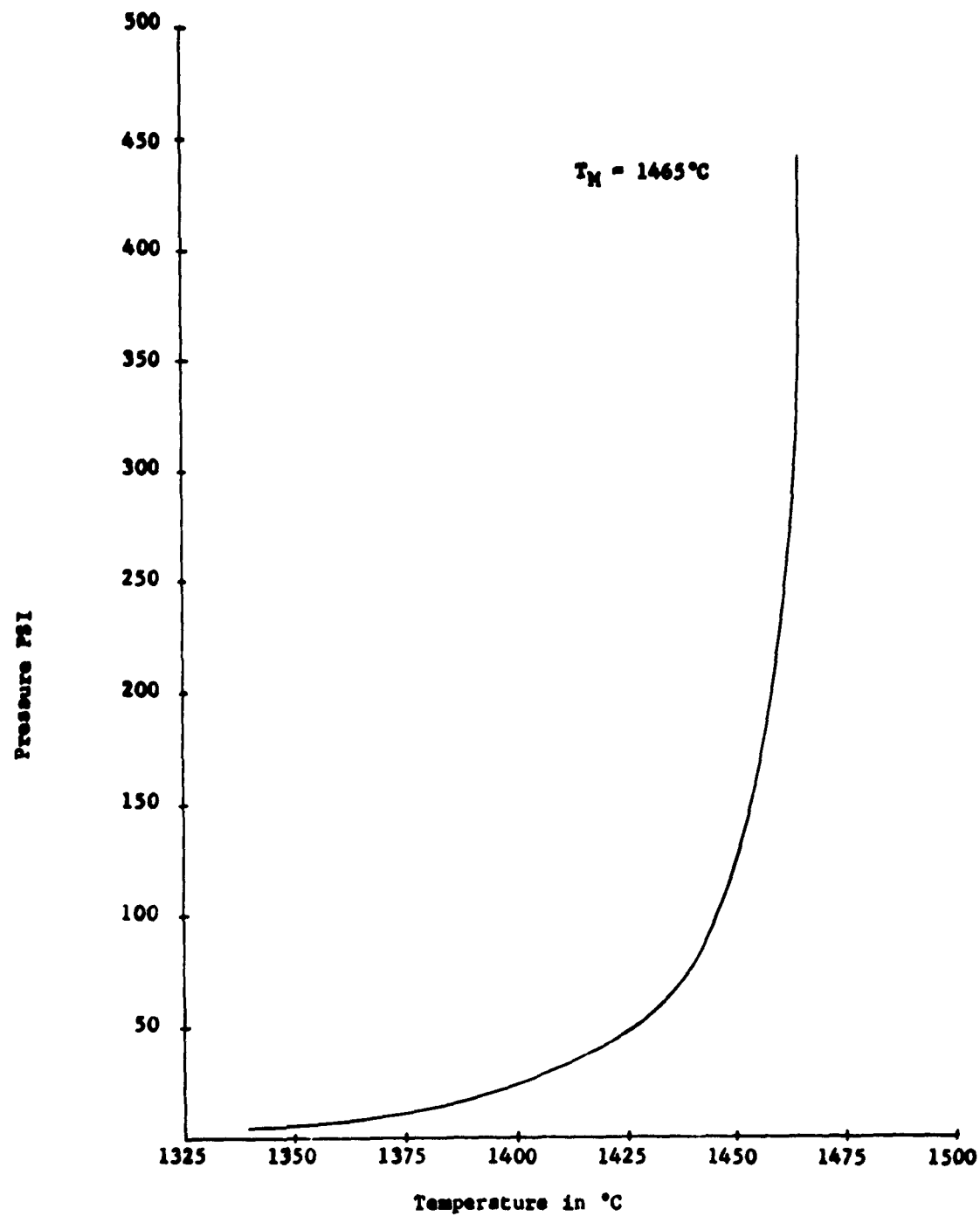


Figure 8. Dissociation Pressure of GaP.

Table VII illustrates the specific steps of the melt growth technique and is typical except for minor variations.

TABLE VII

Sequence and Steps in Melt Growth of GaP Ingots.

1. Prepare ampoule, including GaP charge and excess phosphorus equivalent to 10 atmospheres phosphorus vapor as P_4 at 1500°C.
2. Assemble sleeve, shield and pedestal in furnace. Purge and pressurize to 375 P.S.I. of Argon.
3. Heat rapidly to slightly above melting point (approximately 1540°C).
4. Hold stabilized temperature for 1 hour (pressure thermal increase to 575 P.S.I.).
5. Begin pulling ingot at 0.015 inches per hour. Simultaneous gradual reduction in heater power (2% per hour - for 1 hour).
6. Completion of pull, begin rapid cooling (30% per hour - for 1 hour).
7. Power off for furnace cooling.
8. Release pressure slowly.
9. Remove crucible assembly.

Some minor variations in pull rate, holding time, etc., were done to ascertain minimums and optimums of each. Since the ampoule is housed in graphite and tungsten carbide sleeves a minimum of 30-minutes is required to reach temperature equilibrium. Shorter time resulted in failure to achieve a melt. More homogeneous melts appeared to result from a 1-hour period. Excess phosphorus pressure was explored to 20 atmospheres. As yet, we are unable to correlate any specific difference in results with change in phosphorus pressure above 10 atmospheres.

Some discussion of the pressure environment within the ampoule is of interest. Table VIII indicates the pressure situation at selected intervals during the melt cycle. Actual pressures listed are approximations, of a calculated nature, and not intended to be rigorously accurate. Testing of evacuated empty quartz ampoules indicate they withstand external pressures at room temperature, up to 600 P.S.I. safely when contours are smoothly rounded. Table VIII assumes the included phosphorus is to produce 20 atmospheres at 1500°C.

TABLE VIII
AMPOULE PRESSURE AT INTERVALS DURING MELT CYCLE

<u>Time</u>	<u>Temp. °C</u>	<u>Argon P.S.I.</u>	<u>Pressure on Ampoule P.S.I.</u>	<u>Pressure Inside Ampoule</u>
Start	Room	375	+375	None
Heat up Interval	~1000°C	375	+175	Phos. vapor of 200 P.S.I.
Approach to M.P.	~1480°C	*450	+25	Phos. 300 P.S.I.; GaP 125
During melting	1520°C	*500	0 ± 25	P + GaP ~ 500 P.S.I.
Cooling Down	1400°C	*575	+175	P = 300, GaP = 100
Further Cooled	1200°C	*575	+350	P = 200, GaP = 25

* Pressure increase due to heating of argon in furnace.

At room temperature it is indicated the quartz ampoule is subject to safe pressures. Upon heating the differential pressure decreases in amount until at the melt-equilibrium portion of the cycle, little pressure differential exists. Generally some expansion of the quartz ampoule occurs at this point. However, upon cooling, the furnace temperature lags behind the cooling crucible, and the external pressure produces a squeezing force

which usually collapses the upper portion of the ampoule. When an individual run is controlled accurately, this contraction does not extend to the ampoule portion holding the ingot. This contraction is advantageous in that it affords decreasing volume in the ampoule at the high temperature and prevents decomposition to a significant degree. Upon cooling below 600°C the quartz assumes the typical white, devitrified appearance. Devitrification results in cracking, and it is therefore common to smell phosphorus in the exhaust gas when this temperature is passed.

Figure 9 illustrates the appearance of ingot, ampoule and graphite sleeve immediately after removal.

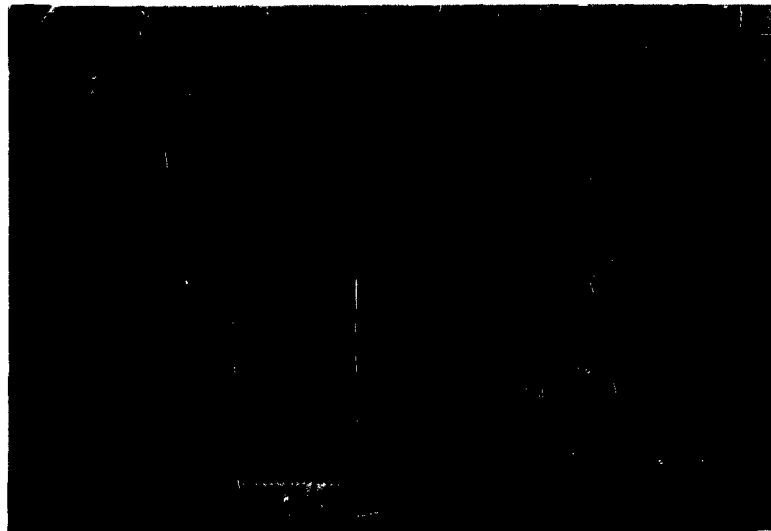


Figure 9

GaP Ingot, Ampoule and Sleeve after Melt Cycle

Figure 10 illustrates ingot M-3 as removed from the ampoule. Photography is by transmitted light. It is encouraging that the ingot, and others, were clear and relatively free of inclusions. This was not true of all ingots, but a large percentage were of this nature.

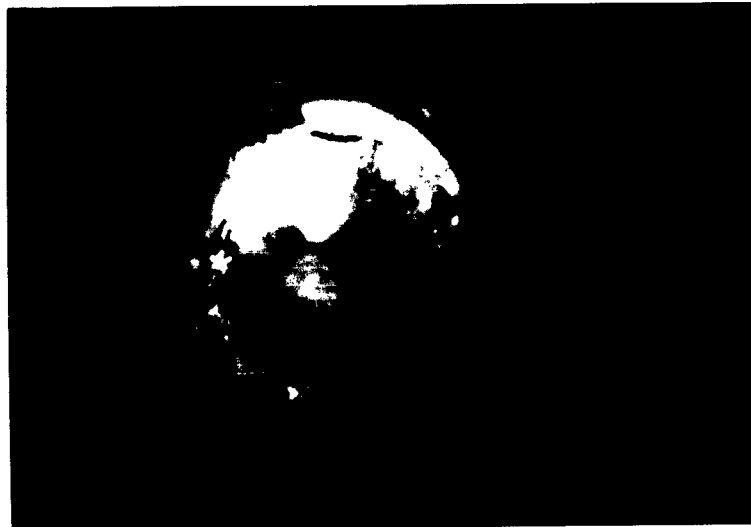


Figure 10. GaP Ingot by Transmitted Light.
(Slices were sawed from this ingot and polished by manual lapping)

Figure 11, photographed by transmitted light illustrates the clarity and freedom from inclusions. The ingot was composed principally of three twinned crystals. Some enlargement is present in both Figure 10 and Figure 11.

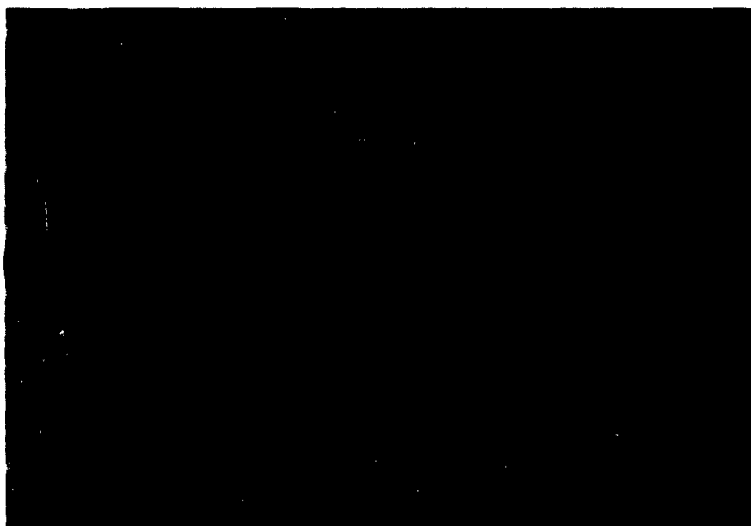


FIGURE 11. Slices of GaP by Transmitted Light. (Enlarged)

Some ingots contained inclusions, principally free gallium. These resulted when the synthesized GaP used for the charge contained unreacted Ga_2O_3 . The free gallium appeared regularly to segregate to the top of the ingot during growth.

Figure 12 illustrates M-8 which had no inclusions, but was multi-crystalline, and M-9 which had severe inclusions in the top layer.



Figure 12
GaP Ingots M-8 and M-9

Sawed slices exhibit the inclusions in the top of M-9, as depicted in Figure 13. It is worth noting that the crystallites increase rapidly in size from the bottom.



Figure 13
Slices of GaP Ingot M-9 (Top) and M-8 (Bottom)

Ingot M-8, which was clear and transparent, but of multi-crystalline structure may be presented conservatively as the median of results attained. Spectrographic analysis of synthesized starting charge, of the included excess phosphorus, and of the ingot may be compared in Table IX. This does not represent the best ingot purity; total impurities in the best ingot analyzed was less than 2 ppm.

TABLE IX
SPECTROGRAPHIC ANALYSIS OF INGOT M-8 (ppm.)

	<u>Si</u>	<u>Mg</u>	<u>Fe</u>	<u>Al</u>	<u>Cu</u>	<u>Ca</u>	<u>Sn</u>	<u>Pb</u>
GaP Synthesized Charge OF-11	10	5	3	10	1	20	*ND	ND
Included Phosphorus Q-004	40	4	1	5	2	10	5	ND
GaP Ingot M-8	100	30	2	20	1	50	*ND	5

* "ND" = Not Detected

The indication in broad context in Table IX is that the overall impurity levels, with the exception of silicon, are largely dependent on the charge and phosphorus used to produce the phosphorus atmosphere. Higher impurity levels have been observed, particularly in silicon, magnesium and calcium. The higher levels appear related to the presence of unreacted components in the charge, and/or excessive melt temperatures. Slices of ingot M-8 were also submitted for X-ray study. Debye Scherrer analysis gave unit cell edge lengths of $5.4505 \text{ \AA}$. This is in exact agreement with published reference values⁽³⁾ of $5.4505 \text{ \AA}$ (Giesecke and Pfister). The largest deviation in such measurements made thus far on melt grown ingots has been $5.4511 \text{ \AA}$. It is indicated that the ingot stoichiometry is very good, with no decomposition phases.

Back reflection Laue patterns were made of the same slices of M-8. Figure 14 illustrates the pattern, made with the beam normal to the surface

of the slice. The spots are near circular, indicating well crystallized, strain free material. The wafer surface is observed to be inclined to the major face normals by 12° from the 1:1:0 plane and 26° from the 1:1:1 plane.

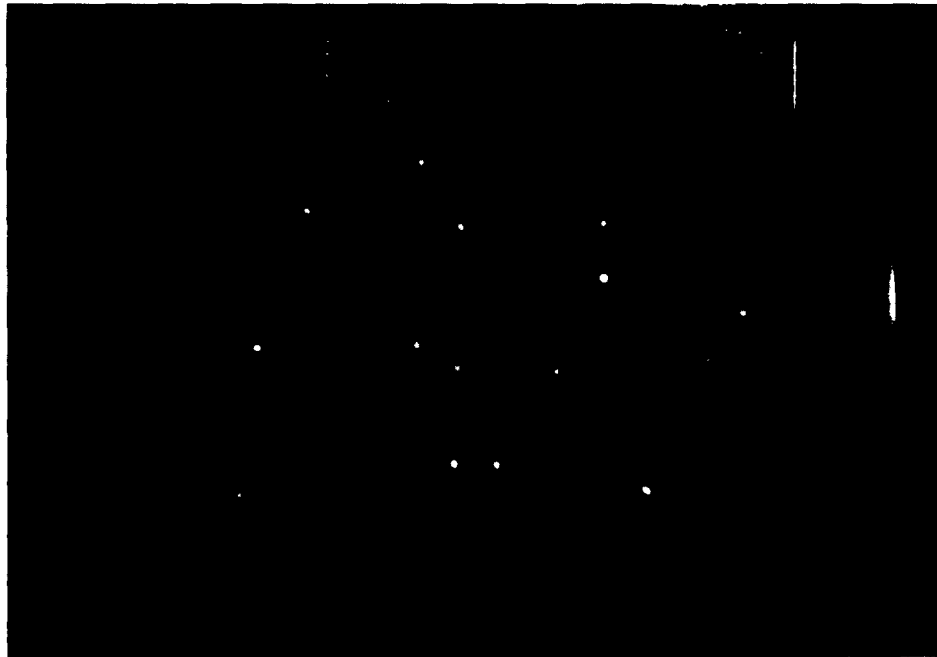


Figure 14

Laue X-ray Pattern of Ingot M-8 Specimen

For comparison purposes, similar X-ray analysis was made of a slice, free of inclusions, of Ingot M-9. Debye Scherrer measurements gave unit cell dimensions of $5.4500 \text{ \AA}$. Laue pattern was similar to that of M-8 with surface inclined by 11° from the 1:1:0 and 32° from the 1:1:1 plane. Spots again were circular and clean.

Mention was previously made of gallium inclusions. The gallium was observed as inclusions in the top surfaces, and a thin, occasional coating of the outer periphery. Some evidence indicates this gallium to be related to incomplete synthesis of the starting materials, aggravated by excess melting temperatures. The presence of gallium in or on the ingot appears related also to high silicon contamination (of the order of 100 ppm). These data are presented in an effort to demonstrate both extremes of analysis.

Several runs were made which were aborted due to furnacing difficulties, poor quartz welding or other causes. These totaled four failures, and are considered misfortunes avoidable with experience and refinement of technique.

Summarizing, the melt growth technique appears practical, and capable of producing device quality GaP. Contamination is not the severe problem anticipated, and minimizing impurities may be expected at an optimum time-temperature combination. Material evaluation indicates very good structure and homogeneity, free from strains, etc. The overall prognosis is very good.

D. VAPOR PHASE CRYSTAL GROWTH*

As a result of previous work on growth of large single crystals of III-VI compounds, it was considered feasible that this technique might be employed to grow large crystals of GaP. The vapor phase growth method used was essentially the sublimation of the GaP charge and subsequent recrystallization on a suitable substrate positioned at a slightly cooler location in the furnace. The technique consists of the following steps:

- (a) Preparation of the GaP by the open flow synthesis of Ga_2O_3 and elemental red phosphorus in an atmosphere of H_2 .

* This work performed by J. Budiselle

(b) Charging into a fused silica ampoule followed by sublimation and recrystallization on a polished fused silica seed plate or plates.

STARTING MATERIALS

All of the GaP used as charge material was synthesized in this laboratory by open flow synthesis as previously described. Several attempts were made at sintering the GaP into an ingot suitable for use as a charge for the crystal growing process. The GaP was placed in a fused silica boat or packed into a fused silica tube. This container was then placed in a fused silica combustion tube in a globar type furnace. After placing the charge in the furnace the entire system was evacuated to <1 micron of Hg and purged four times with high purity dry argon. The temperature was then raised to 750°C and held there for two hours under a vacuum of <1 micron of Hg. The temperature was then increased to 900°C for one hour still under high vacuum. Upon reaching 900°C a dark deposit was formed in the cooler portion of the quartz combustion tube downstream from the GaP charge. This deposit was found to be Ga and P indicating partial decomposition of the charge. Due to this decomposition the sintering process could not be carried out successfully under vacuum conditions. Accordingly the GaP was packed into the tube without prior sintering for the vapor deposition.

EQUIPMENT

A globar type furnace capable of operating at 1400°C is employed for the crystal growth process. The furnace has elements with an effective heating length of 10 inches. A profile of the temperature gradient is shown in Figure 15 with the center temperature at 1250°C and 1300°C.

The temperature of the center of the furnace is monitored by use of a Pt-Pt 13% Rh thermocouple with an indicating pyrometer.

The combustion tubes used for crystal growth runs are mullite "triangle H-5" open both ends, 2 inches o.d. by 1½ inches i.d. and 48 inches long. These tubes are recommended to be vacuum tight at 1700°C under continuous operation, and have proved to be very satisfactory. The open ends of the tube are sealed vacuum tight by means of a Garlock ring type seal against a metal plate. Connections to vacuum pump, inert gas and pressure gauge are made through this plate.

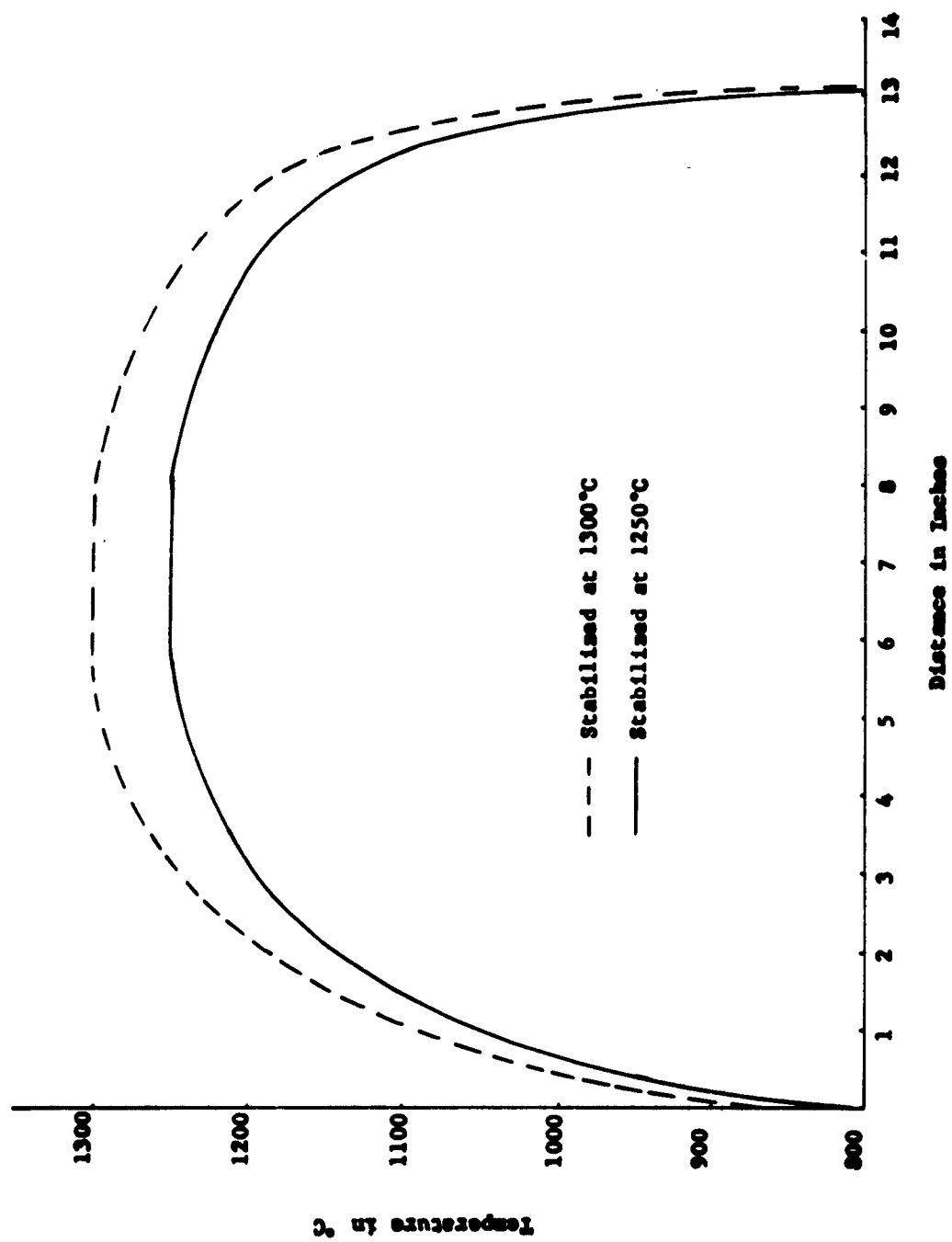


Figure 15. Temperature Profile of GaP Crystal Furnace.

CRYSTAL GROWTH

Nine vapor phase crystal growth runs were carried out during this quarterly work period, numbering JB-1 thru JB-9.

The first and initial run was carried out at 1250°C under 15 mm pressure of argon. The apparatus is illustrated in Figure 16. The system consists of a 3/4 inch i.d. clear fused silica tube 8 inches long with a clear fused silica plate 3/4" D. x 1/16" thick welded on one end. This seed plate is designated as the primary seed plate. The other seed plate is of the same material, made so that it may be positioned after the boat containing the GaP charge has been placed in the tube. This seed plate is designated as the secondary seed plate.

The charge used in this run weighed 9.5 grams and was taken from synthesis run OF-10. Growth was carried out for 36 hours after reaching a stabilized temperature of 1250°C. When the run was taken apart, a deposit approximately 3/4" diameter x 1/16" thick had been formed on the primary seed plate. This platelet was very polycrystalline and dark in color, practically opaque. A mineral deposit had formed on the secondary seed plate. Upon further investigation, free Ga was found as a residue of the charge, and a deposit of P was found in the cooler portion of the mullite combustion tube. The indication is clearly that decomposition of the GaP charge occurred. This decomposition agrees with the curve of dissociation pressure of GaP shown in Figure 8.

1. Mullite Tube.
2. Globar Heating Elements.
3. Secondary Seed Plate.
4. GaP Charge Boat.
5. Primary Seed Plate.
6. Furnace.
7. Center of Furnace.

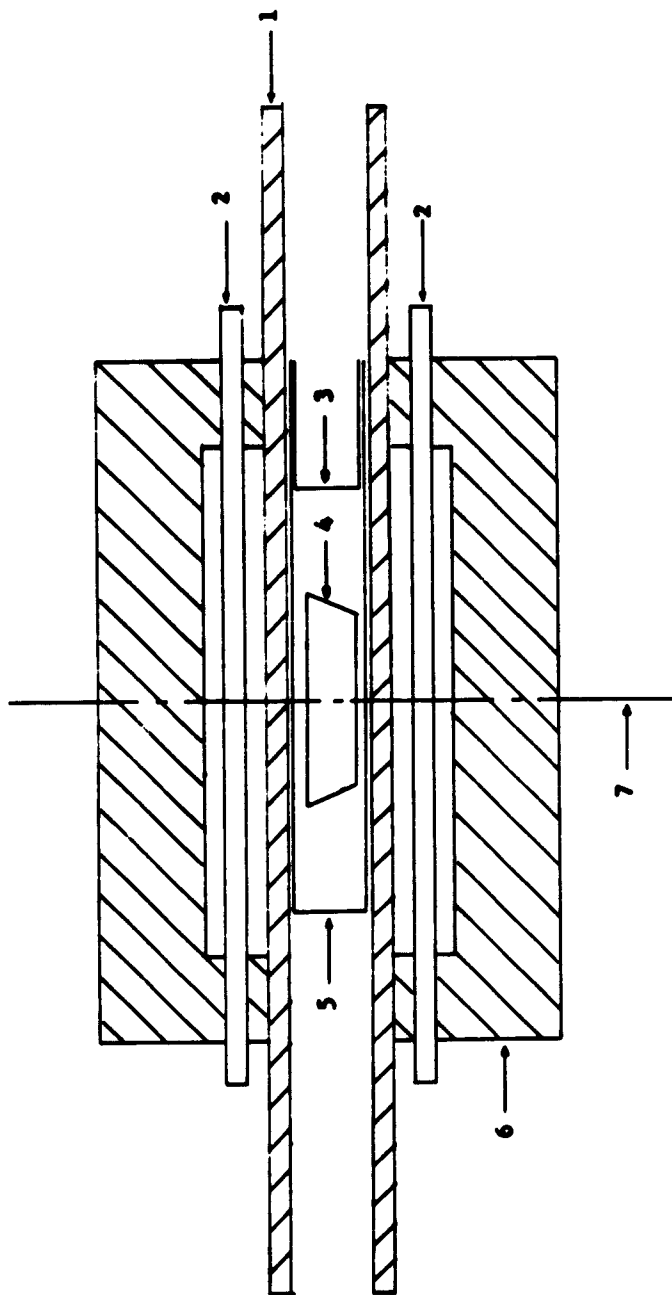


Figure 16. Vapor Phase Growth Apparatus.

It was then decided that future runs would have to be made under a pressure of one of the constituent elements (phosphorus) and at 1300°C. This higher temperature should promote better crystal growth. In order to do this the crystal growth would preferably be carried out in a sealed ampoule of fused silica. The ampoule in turn should be placed in a protective sleeve to prevent it from expanding against the walls of the mullite tube. The substance most readily available and with suitable strength was graphite, therefore a sleeve of graphite 1 inch i.d. by 1½" o.d. and 10 inches long and having press fit end plugs was fabricated.

The sealed ampoule technique was employed using a double primary seed plate. The second primary seed plate is slotted on the edge to permit evacuation and purging of the ampoule with argon after loading. The ampoule is evacuated to 1 micron and purged with argon four times before sealing off. Figure 17 shows this arrangement with graphite sleeve.

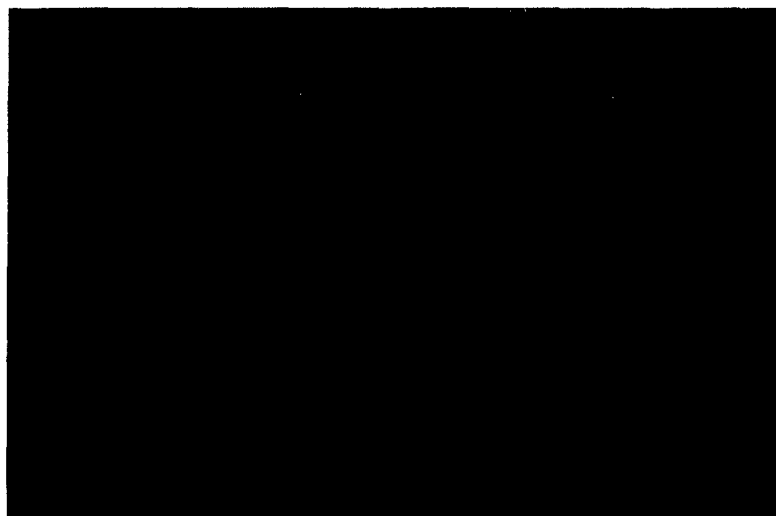


Figure 17
Vapor Phase Growth Sealed Ampoule and Graphite Sleeve

The starting charge material was four grams from synthesis run OF-12. A picture of this crystal plate is shown in Figure 18. The deposition temperature of the seed plate was approximately 1200°C. The run duration was 96 hours. The plate is flat on the bottom, but has many beautiful pyramidal crystals forming an irregular upper surface. The largest of these crystals is approximately 4 mm by 5 mm.

Picture #1374

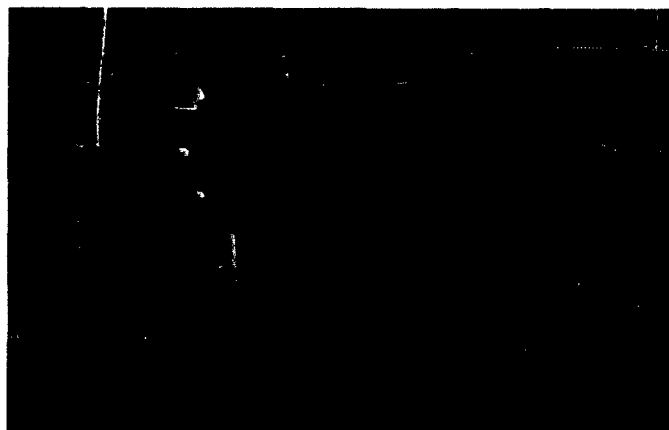


Figure 18
Crystal Plate from JB-4

This plate was submitted as a sample for X-ray analysis. An attempt was made to obtain a back reflection Laue pattern with the beam approximately normal to one of the larger pyramidal faces which was perhaps 4 mm in width. The Laue pattern is shown in Figure 19. The pattern obtained showed that the beam was inclined about 9° from the normal to the (111) face and towards the (112) plane. The pattern indicates good crystallinity with absence of strain or twinning.

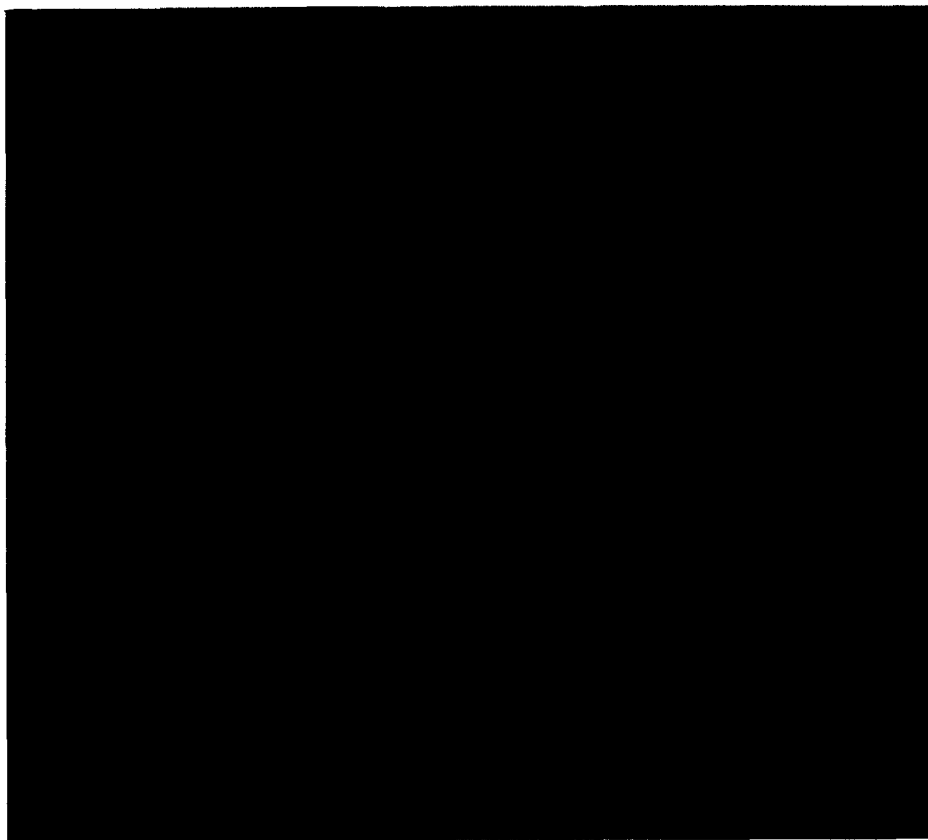


Figure 19

Laue Pattern of Crystals from JB-4

A small fragment of the GaP was removed and ground for a powder pattern specimen. The unit cell edge length was found to be $5.4511 \text{ \AA}$ as compared to the reference value of Giesecke and Pfister⁽³⁾, $5.4505 \text{ \AA}$.

Samples of these crystals were also sent to the spectrographic laboratory for complete impurity analysis. Results are shown in Table X, both as starting charge from synthesis OF-12 and the crystals grown.

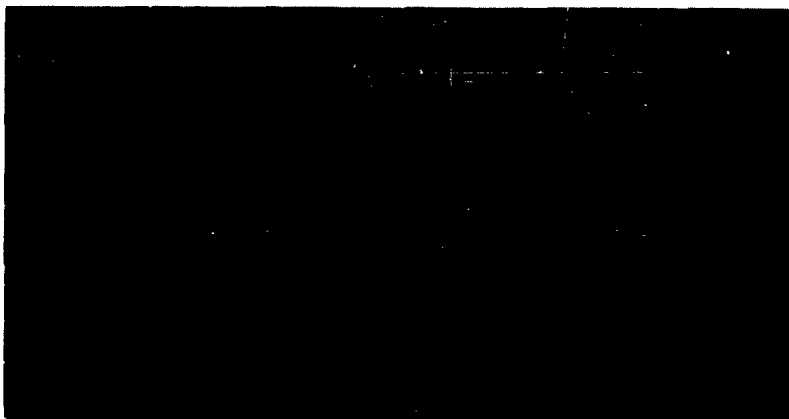
TABLE X

IMPURITY ANALYSIS OF VAPOR PHASE CRYSTAL

Reference No.	Sample Description	Impurities in ppm						
		B	Si	Mg	Fe	Al	Cu	Ca
M6302AB	Starting Charge OF-12	10	50	3	2	5	2	10
M6302AV	Crystals from HB-4	0	300	10	40	0	2	30

It is indicated that some increase in silicon and iron content occurred. However, the magnitude of these are small enough that it should be possible to eliminate this contamination.

An attempt to duplicate run JB-4 was made in run JB-5. These crystals are shown in Figure 20. The starting charge was 5 grams of GaP from synthesis run OF-13. This run was carried out the same as JB-4. These crystals are not nearly as large as those from JB-4. The ampoule in this run had expanded from internal pressure against the graphite sleeve. Even though this run was also for 96 hours, there was considerable unused charge, which can be seen in the center of Figure 20. This remaining charge can be explained by the high internal pressure of the ampoule which would have depressed the sublimation rate of the GaP charge. Spectrographic data are not available on this run at the present time.



Several of the other runs produced informative and interesting results. One, particularly, produced a primary plate of beautiful pyramidal crystals, transparent, of yellow orange color. Crystallites up to 5 mm per side were observed.

In summary, the vapor phase approach appears worth further study. The method produces stoichiometric, strain free crystals, admittedly small thus far. The crystalline structure is good, and contamination problems are not so severe as to preclude this form of growth. The results are particularly good, when judged in the light of size of beginning charges. This method works best when large volumes of charge are transported slowly over long periods. Charge size thus far has been restricted to a few grams. It is important to note that decomposition has been avoided entirely, even over periods of 96 hours, at this high temperature. It is particularly useful, since work time is used only when "setting up" and stabilizing the furnace.

DEVICE FABRICATION

Device fabrication is currently under study but in the early stages. Since cleaning and surface preparation inevitably becomes significant to device performance, attention was focused first in this area. The common III - V etchants were found ineffective, or very slow in either cleaning or polishing. This group includes $\text{HF-H}_2\text{O}_2$ solutions; $\text{KOH-H}_2\text{O}_2$ solutions, methyl alcohol and bromine and dilute HF-HNO_3 solutions. The best cleaning and polishing etchant was found to be methyl alcohol saturated with chlorine gas by bubbling during use. This solution is used in a rotating polisher built in house for this purpose. Figure 21 illustrates the device.



Figure 21
Chemical Polishing Device

The top structure houses a 3 speed reversible motor assembly, hinged, arranged to drive a plastic cylinder at the end of the shaft extension. Specimens are mounted on the bottom face of the cylinder with low temperature adhesive wax. The etchant solution in a low form beaker is stirred magnetically by a Cenco magnetic stirrer. Rotation of the specimens is counter to the fluid movement, at the outer periphery of the container. Periods of the order of 5 to 20 minutes suffice to remove damaged surface layers on the GaP specimens and produce a highly polished surface. This polish is uniform across twin-boundary lines, but produces a noticeable contrast with crystallites of different orientation. Cleaning is preferably done immediately before use of the specimen and is followed by thorough rinsing in de-ionized water and alcohol.

Contacting such a polished surface has been accomplished by plating with indium followed by alloying of gold foil dots placed on the indium plated area. The indium is alloyed for 1 minute at 450°C in a hydrogen atmosphere, followed immediately by gold alloy at 650°C for 1 minute. Penetration depths are yet to be measured. These contacts are mechanically sturdy and ohmic. The contact is considered capable of temperatures in the 500°C range.

V. SUMMARY

The synthesis of GaP by the open flow system described is practical and although ultimately another, better method may be developed, has supplied material of reasonable purity for the melt growth of GaP ingots. Melt growth of GaP ingots has been accomplished. The material is of excellent crystal structure and stoichiometry. Ingots generally are comprised of 2 or more large crystallites, of twinned nature, having few or no inclusions. Impurity levels are fairly low and can be reduced. Stoichiometry is good, as defined by Debye-Scherrer lattice constants. Uniformity, reproducibility and yield rates of the melt growth techniques are good and may logically be expected to improve.

Vapor phase growth of GaP crystals of excellent crystal lattice structure and stoichiometry was accomplished. Individual crystallites of 5 mm per side were observed. The size is impressive when viewed in the light of the initial charge size. This work has shown empirical agreement with published data on decomposition pressures of GaP in the 1300°C range. A chemical polishing technique suitable for GaP has been established. The etch-polish solution found most effective is methyl alcohol saturated with chlorine gas. Rotation of specimens is found desirable. Alloy contacting using an alloy of indium-gold has been explored and is expected to provide good contacting at elevated temperatures. Junction and device fabrication studies have begun, but as yet are in the early stages.

VI. FUTURE STUDIES

Future studies are to include, in scope, effort in all major categories of the investigation. The synthesis technique will be refined, with particular emphasis on purity, aggregation of particle and/or needle size, increased yield, and volume per run.

The melt growth program is to be expedited and improved. Attention will be focused on purity, crystal homogeneity, increased size, and single crystal structure. To date, cooling and growth rates have been rather rapid. As the uniformity and quality of the synthesized material is improved, a careful study of crystal structure as a function of growth rate is intended.

Since the vapor phase process shows good promise as a method for growing larger crystals of GaP suitable for device fabrication, this process will be further studied during the forthcoming quarterly work period. Special emphasis will be to determine optimum conditions for growth or larger clearer crystals. Particularly deposition temperature and phosphorus pressure used will be studied. Emphasis will be on growth of crystals of higher purity.

A study of the efficiency of doping the bulk material during synthesis, and doping during melt growth is planned. It is intended to provide a reproducible method of obtaining doped GaP of predictable type and resistivity.

Material evaluation studies are planned to include determination of type, resistivity, mobility, lifetimes and optical transmission characteristics. Several of these parameters will require large area single crystal specimens and thus will be contingent on the progress of the materials program.

Device fabrication studies include further exploration of contacting techniques; fabrication of alloyed junctions, diffused junctions and epitaxially grown junctions, and eventually three terminal devices.

Device evaluation studies are intended to establish diode characteristics, temperature performance and electro-luminescence parameters. When three terminal devices are fabricated, evaluation of transfer characteristics will be carried out.

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VIII. PERSONNEL

Engineering Time Expended from December 14, 1962 to, and including March 14, 1963:

Allen, Harold L.,	19 Hours
Ames, William A.,	6 "
Brown, Lloyd W.,	149 "
Budiselic, John C.,	138 "
Roderique, J. S.,	176 "
Starks, Ralph J.,	152 "
Stone, Louis E.,	96 "

Total, 736 Hours.

LES/tp.

AD _____	Accessories No. _____	UNCLASSIFIED	AD _____	Accessories No. _____	UNCLASSIFIED
The Eagle-Picher Company, Chemicals & Metals Division, Miami, Oklahoma. GALLIUM PHOSPHIDE DEVICES, L. E. Stone, J. R. Musgrave, et.al. First Quarterly Technical Report Dec. 14, 1962 to March 14, 1963 53 pp - Illustrations & Graphs, Gallium Phosphide Synthesized, Melted; Impurity Analysis of Materials and Products. Description Techniques, Apparatus.		1. Gallium Phosphide 2. Gallium Phosphide Devices. 3. Contract Nr. DA-36-039-AMC-00103(E)	The Eagle-Picher Company, Chemicals & Metals Division, Miami, Oklahoma. GALLIUM PHOSPHIDE DEVICES, L. E. Stone, J. R. Musgrave, et.al. First Quarterly Technical Report Dec. 14, 1962 to March 14, 1963 53 pp - Illustrations & Graphs. Gallium Phosphide Synthesized; Melted, Impurity Analysis of Materials and Products. Description Techniques, Apparatus.		1. Gallium Phosphide. 2. Gallium Phosphide Devices. 3. Contract Nr. DA-36-039-AMC-00103(E)

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L. E. Stone, J. R. Musgrave, et.al.	2. Gallium Phosphide Devices.		L. E. Stone, J. R. Musgrave, et.al.	2. Gallium Phosphide Devices.	
First Quarterly Technical Report Dec. 14, 1962 to March 14, 1963 53 pp - Illustrations & Graphs,	3. Contract Nr. DA-36-039-AMC-00103(E)		First Quarterly Technical Report Dec. 14, 1962 to March 14, 1963 53 pp - Illustrations & Graphs.	3. Contract Nr. DA-36-039-AMC-00103(E)	
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