SECOND QUARTERLY TECHNICAL REPORT

Report Date: July 14, 1963

March 14, 1963 to June 14, 1963

"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

SECOND QUARTERLY TECHNICAL REPORT

Covering the Period

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"GALLIUM PHOSPHIDE DEVICES"

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Research Laboratories,
Miami, Oklahoma.

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The work performed under this contract was made possible by the support of the U. S. Army Electronic Materiel Agency, 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 appropriate devices.

The materials category includes the selection of a suitable synthesis process, growth of single crystals of best purity, and refinements in technique for optimum purity, stoichiometry and crystalline structure. Suitably doped n-type and p-type gallium phosphide is considered a principal objective.

The evaluation program includes the analysis of impurity concentrations, measurement of resistivity, Hall mobilities and similar electronic parameters. Optical properties such as transmittance, absorption, and electroluminescence are included.

The fabrication program is aimed primarily at single junction diode structures, although three terminal devices are contemplated as a logical extension in evaluating the junction parameters. Device parameters of interest include contact ohmicity, I-V rectification properties, temperature performance, junction luminescence and photovoltaic effects. Three terminal evaluation in terms of transfer characteristics is considered an objective. Further parameters of special interest will be carried out when considered useful by the Government Contracting Officers Representative.

II. ABSTRACT

The synthesis of gallium phosphide has been improved in purity of product, recovery efficiency, and reproducibility. Careful control of process temperatures and flow rates has been a major factor in this improvement and exploits the inherent purification of the phosphorus. Alternative vapor synthesis systems have been explored without practical success.

The melt growth was impeded by furnacing difficulties, which have been resolved, and melt growth studies are being pursued.

Epitaxial growth of gallium phosphide layers of superior quality has been accomplished using iodine transport in both sealed ampoule and open-flow techniques. The latter offers significant advantages in facilitating alternate type growth and close control of thickness.

Diffused, alloyed and epitaxial gallium phosphide diodes have been fabricated and tentative evaluation carried out. Some resistive effects were observed, and are considered principally the effect of material properties.

Evaluation of optical properties of early bulk gallium phosphide material has been carried out. Results closely agree with theoretical physical properties.

III. PUBLICATIONS, REPORTS AND CONFERENCES

Reports:

Monthly Letter-Type Report No. 3 was prepared and delivered on 4/20/63.

Monthly Letter-Type Report No. 4 was prepared and delivered on 5/16/63.

Conferences:

A conference was held at Fort Monmouth, New Jersey, on May 23, 1963. Present were Messrs. Robert Yatsko, Phillip Newman and James Kesperis, of Evans Laboratory, and Mr. Louis E. Stone of this laboratory. The subject of the conferences was the current progress of the investigation, and delivery of the following samples:

M6305-AZ = Epitaxial GaP on GaAs Substrate EG-36-2
M6305-BA = Epitaxial GaP on GaAs Substrate EG-35-2
M6305-BB = GaP diode ELGD-2-1

A conference was held at the Eagle-Picher Laboratory, Miami, Oklahoma, on June 5 & 6, 1963 with Mr. Robert Yatsko of Fort Monmouth, New Jersey. The techniques for open-flow gallium phosphide synthesis, melt-growth of crystals, epitaxial growth, chemical polishing, microscopic measurement, etc., were demonstrated in detail. A comprehensive discussion of purpose and guidelines for the investigation was held and current progress and problems discussed.

Specimen M6306-AT, polished cross-section of an epitaxial gallium phosphide layer on gallium arsenide substrate was delivered to Mr. Yatsko.

IV. FACTUAL DATA

A. Introduction:

Satisfactory progress has been made in the open-flow gallium phosphide synthesis phase during this period. As will be detailed subsequently, product purity levels have been improved; reproducibility from run-to-run has been steadily increased; less variation in yield is noted, and use of less pure phosphorus without increased contamination has been possible by careful control of its sublimation temperature.

Several alternate synthesis techniques have been explored briefly, with little success. These were planned to use vapor sources for both the phosphorus and gallium, reacted in a high temperature zone. Both produced very low yields and were judged impractical.

The melt growth phase was temporarily impeded during this period. The thermal insulation in the high temperature furnace was replaced with a better material. The improved properties of this new and different insulation has produced a quite sharp temperature gradient within the melt zone, and made necessary a series of test runs to establish the proper temperature and pull rates. Several unsuccessful runs were made before it became apparent that an increased vertical temperature gradient existed. Orderly and logical tests have now been made, and tentative operating parameters have been established. It is considered that melt grown ingots of good crystal structure will be forthcoming soon.

Slices of melt grown ingots have been used for evaluation and devices. This material is of multi-crystalline nature, undoped, and of low net

"n" carrier concentration. Spectral transmittance and infrared absorption data are included as part of this report.

The device fabrication phase has proceeded satisfactorily. Principal effort has been on epitaxial growth of gallium phosphide layers on gallium arsenide substrates, and a small numberof bulk gallium phosphide alloyed diodes. The epitaxial growth has included "n" gallium phosphide on "n" gallium arsenide, and "p" gallium phosphide on "n" gallium arsenide. Clear single crystal layers of from eight to eighty microns thickness have been grown. Significant photovoltaic measurements have been made on some of these specimens.

B. Gallium Phosphide Synthesis*:

The synthesis of gallium phosphide is accomplished by the open-flow technique, described in detail in the First Quarterly Report[1]. Briefly stated the method involves passing elemental phosphorus vapor over gallium sesquioxide at an elevated temperature, using hydrogen gas as a carrier. The quartz environment gives rise to the principal contaminant, silicon.

The Ga_2O_3 used is high purity material, obtained from the Eagle-Picher Company. Total impurities range from 0.7 PPM to 1.01 PPM, of which the major component, silicon, ranges about 0.5 PPM.

Original synthesis runs[1] indicated very high phosphorus impurities were present and were carrying over into the final product. Very high purity phosphorus was obtained (1.0 PPM total), and sublimation temperatures carefully controlled. Spectrographic analyses of twenty-two runs made during

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* This phase of the work was performed by J. S. Roderique.

the first quarter are summarized in Table I.

TABLE I

Summary of Spectrographic Analysis (Previous)

	Impurities in Parts Per Million						Total Impurities (PPM)
	Si	Mg	Fe	Al	Cu	Ca	
GaP av. Imp.	50.0	3.0	1.0	2.0	1.0	10.0	67.0
Best (OP-15)	7.0	3.0	N.D.	2.0	N.D.	N.D.	12.0

NOTE: "N.D." = None Detected.

The inherent purification obtained in subliming the phosphorus under careful temperature control was observed by analysis of total phosphorus impurities before use, and analysis of the heel remaining after terminating a run. This effect is illustrated for high purity phosphorus in Table II, as noted in the First Quarterly Report.

TABLE II

Summary of Spectrographic Analysis of Phosphorus and Heel.

Phosphorus	Run Number	Total PPM Before Sublimation	Total PPM Heel
Fisher,	OP-8	7×10^5	2×10^5
AACC Q-004,	OP-11	N.D.	6.0
AACC Q-003,	OP-13	0.5	10.5
AACC Q-003,	OP-15	0.5	100.0

NOTE: "N.D." = None Detected.

The inference of these data was that careful control of sublimation temperatures should improve final product purity and/or allow use of less pure phosphorus. During this quarter more exploration was carried out to clarify this factor.

Impurity levels in starting materials was carefully monitored by spectrographic analysis throughout this work period. The Ga_2O_3 used was Eagle-Picher high purity semiconductor grade, with impurities as illustrated in Table III.

TABLE III

Gallium Sesquioxide Spectrographic Data.

	Impurities - in Parts Per Million					
Eagle-Picher Lot Numbers	Pb	Cu	Fe	Mg	Ca	TOTAL
137.3,	0.10	0.36	0.10	0.007	0.33	0.977
I.Q - 869,	0.10	0.36	0.10	0.087	0.33	0.977

Phosphorus purity is defined in Table IV. Note that a wide difference exists in bulk impurities. These lots of phosphorus were fresh lots, stored in sealed containers in inert atmosphere.

TABLE IV

Bulk Phosphorus Impurity Spectrographic Data.

	Impurities - in Parts Per Million							
Phosphorus	Si	Mg	Al	Cu	Ag	Ca	Na	TOTAL PPM
AACC Lot Q-005,	20.0	2.0	50.0	1.0	5.0	20.0	N.D.	53.0
AACC Lot Q-023,	5.0	N.D.	N.D.	N.D.	5.0	2.0	N.D.	12.0
Fisher, 701504,	20.0	3.0	5.0	0.5	0.5	500.0	50.0	579.0

NOTE: "N.D." = None Detected.

A surplus of fresh phosphorus was used each run, and a generous heel left at the termination of the run. This residue was analyzed spectrographically to indicate any build-up in impurity concentration. Results, indicated in Table V, were in agreement with the earlier work, and show a remarkable increase.

TABLE V

Residual Phosphorus Impurity Concentrations.

Reference Numbers	Run Numbers	Phosphorus Identity	Impurities - Parts Per Million: Total PPM Before Sublimation	Total PPM Residual Heel
M6304-AE	OF-25	Fisher #1,	1.1×10^4	1.3×10^5
M6304-BH	OF-26	Fisher #2,	500	1.1×10^3
M6304-BI	OF-27	Fisher #2,	500	2.1×10^4
M6304-BK	OF-28	Fisher #2,	500	1.35×10^4
M6305-AR	OF-29	Fisher #2,	500	1.1×10^4
M6306-BI	OF-30	Fisher #2,	500	2.6×10^4
M6306-BJ	OF-32	Fisher #2,	500	2.7×10^4
M6306-BW	OF-33	Fisher #701504,	579	7.8×10^4

It is evident from these data that the sublimation of phosphorus at restricted, controlled temperatures (below 400°C) left the major contaminants in the residue. The next consideration is to what degree this effect is reflected in product purity. Table VI indicates results of spectrographic analysis of the gallium phosphide product. In each case, the product was crushed, mixed and sampled, rather than sampling preferentially the needle formation. Thus these data represent overall purity,

TABLE VI

Synthesized GaP Impurity Analysis.

Impurities - in Parts Per Million

GaP Run	Si	Mg	Al	Cu	Ca	TOTAL - PPM
OF-23	20.0	3.0	7.0	0.5	5.0	35.5
OF-24	30.0	5.0	5.0	1.0	5.0	46.0
OF-25	20.0	5.0	2.0	1.0	5.0	33.0
OF-26	50.0	3.0	N.D.	N.D.	10.0	63.0
OF-27	30.0	3.0	N.D.	N.D.	10.0	43.0
OF-28	50.0	3.0	N.D.	N.D.	5.0	58.0
OF-29	20.0	5.0	N.D.	1.0	5.0	31.0
* -31	300.0	3.0	2.0	1.0	10.0	316.0
OF-32	5.0	3.0	2.0	0.5	10.0	20.5
OF-33	30.0	3.0	2.0	1.0	10.0	46.0
Average, excluding #31, equals,	28.0	3.6	2.0	0.5	7.0	41.8

NOTE: * = This run was a sintering of OF-12, 14-A, and OF-30 material. (Sintered 1000°C - 4 hours under helium, 1000°C - 2 hrs. under hydrogen). This explains the relatively high build-up of silicon.

"N.D." = None Detected.

It is of interest to compare the average values of Table VI with those of Table I, which were carried out the previous quarter using high purity phosphorus with less stringent restriction and control of temperature. The overall average impurities of this quarter are at least as good. It is considered subsequent runs with the higher purity phosphorus will benefit from this study by a further decrease in impurities, with the possible exception of silicon.

Recovery of gallium from the Ga_2O_3 as gallium phosphide was monitored, by comparing the relative weights with calculation of the appropriate mol fractions. Considerable scatter in recovery is observed. The trend has been an increase in recovery percentage. An increase in uniformity of final product has been observed also in recent runs. Figure 1 illustrates graphically the recovery percentage during this work period.

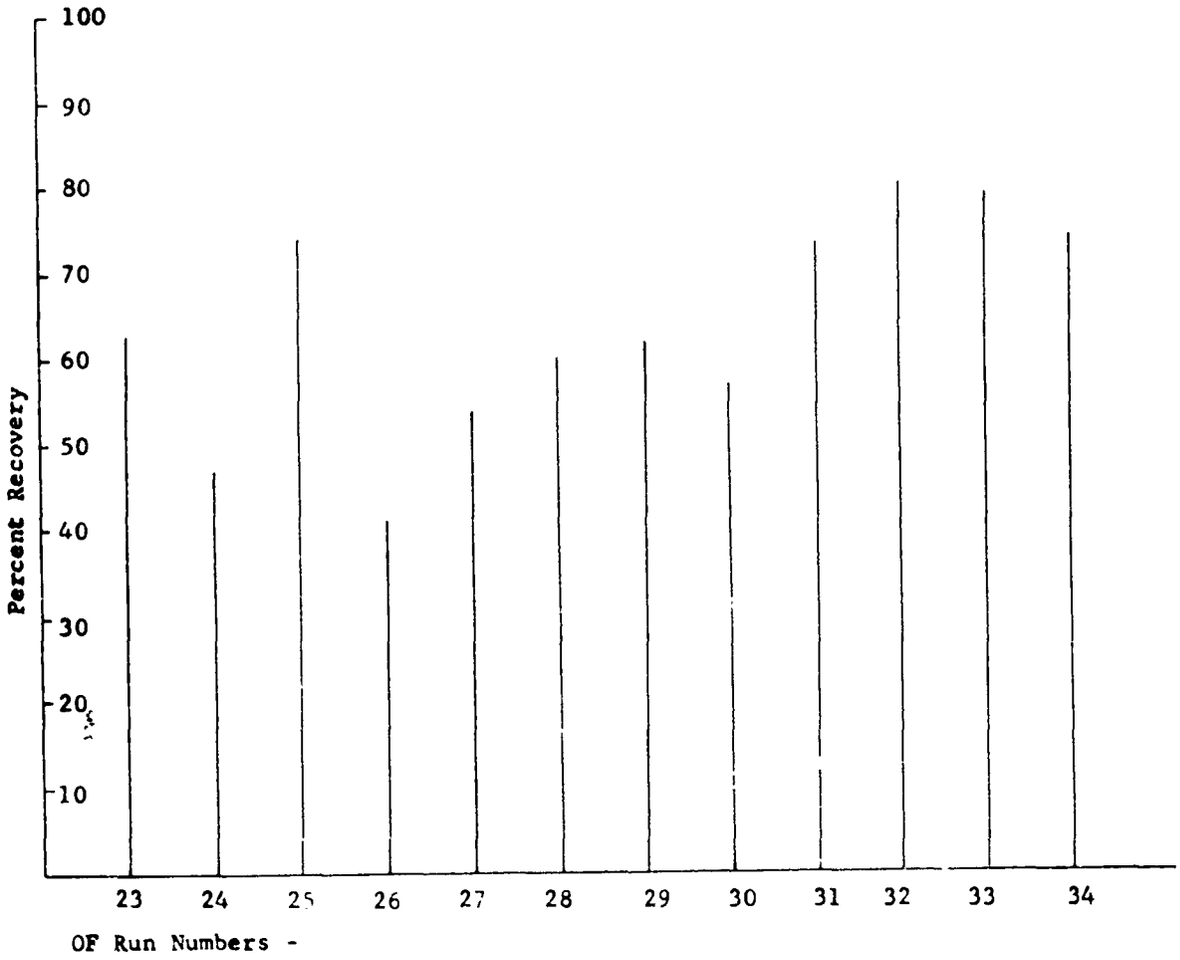

Figure 1. Gallium Recovery as Gallium Phosphide in Synthesis.

Typical GaP product is illustrated by Figure 2 and Figure 3. The direction of H_2 flow may be inferred by the dendritic needle growth. Particular note is made of the uniform color.

Figure 2. Photograph of Gallium Phosphide Product of OF-24.

Figure 3. Photograph of Gallium Phosphide Product of OF-26.

Some improvements in apparatus is being incorporated currently, and are expected to improve both control and product quality.

C. Alternate Synthesis Methods:

The open-flow system previously described is adequate in general, yet leaves something to be desired in (a) volume per run, (b) density of product, and (c) segregation of residues and by-products. Volume of charge is not easily scaled up over 25 grams, without traces of residual unreacted Ga_2O_3. Product density is that of a semi-compacted powder; crystalline aggregate material would be preferable. To prevent inclusion of adsorbed phosphorus, gallium monoxide and other phases, the product and boat are sintered briefly before and after reaction, which reduces the net yield of gallium phosphide.

Thus some exploration of a vapor-vapor reaction was contemplated, which might produce crystalline-aggregate material, and eliminate several of the problems mentioned. Three alternates were suggested and carried out. The first employed gallium trichloride and phosphorus trichloride; the second gallium trichloride and elemental phosphorus vapor; and the third gallium triiodide and elemental phosphorus vapor.

Gallium Trichloride and Phosphorus Trichloride Method:

Since high purity gallium chloride is not available commercially, it was synthesized in our own laboratory. The apparatus used for this purpose is illustrated in Figure 4. A 25-mm quartz tube, horizontal at one end, was arranged to have a sump near its middle, to which a quartz receiver was welded. Chlorine gas, suitably metered and dried, was passed over a quartz boat, containing high purity gallium, which was located in the horizontal section. Appropriate scrubbers, and exhaust apparatus completed the gas train.

Figure 4. Gallium Trichloride Synthesis Apparatus.

The trichloride synthesis procedure is as follows:

A small quartz boat containing 99.9999 percent pure elemental gallium is positioned in the upstream horizontal portion of the reaction tube. The unit was purged with dry chlorine gas for 30 minutes, the flow was adjusted to a slow rate (0.5 LPM) and heat applied with a gas burner to the gallium boat. The reaction, once started, was exothermic and continued after heat was removed until synthesis was completed.

The synthesized gallium trichloride solidified on the downward portion of the reaction tube and was liquefied with a small amount of heat. It was then collected in the quartz receiver.

There was some free chlorine occluded in the gallium trichloride product. The chlorine gas was replaced with helium and at this time the trichlorine product was warmed until liquid, releasing the free chlorine. The trichloride receiver was cut free, sealed and stored until used for gallium phosphide synthesis.

The first effort at synthesizing gallium phosphide from gallium and phosphorus trichloride was carried out in the apparatus pictured below in Figure 5.

Figure 5. Gallium Phosphide Synthesis - From Chloride Apparatus.

The synthesis system consisted of induction heating of a graphite substrate to 600°C (subsequently to 800°C), resistance heated individual $GaCl_3$ and PCl_3 boilers, appropriate drying of helium carrier gas, and suitable scrubbers and exhaust for tail gases. Total helium flow was measured, (0.5 LPM) and then divided and passed through H_2SO_4 bubblers to their respective boilers.

After purging for 30 minutes, helium gas flow was adjusted and the graphite substrate was raised to 600°C. The two chloride boilers were raised 20°C above the boiling points, and the vapor streams combined before passing over the heated substrate. After 30 minutes running time, the process was halted and results observed. Some synthesis had occurred, but the reaction

$$GaCl_3 + PCl_3 \rightleftharpoons GaP + Cl_2$$

appeared heavily unbalanced toward the left at this temperature, resulting in only a small quantity of gallium phosphide.

Considering the possibility of CCl_4 formation from the graphite substrate, it was enclosed in clear quartz and the experiment repeated. Results were essentially the same. A third trial was made at 800°C substrate temperature, which resulted in a smaller quantity of gallium phosphide product.

Gallium Trichloride and Phosphorus Method:

Since the by-product chlorine concentration was considered to weight the reaction equilibrium toward the left, a reduction would enhance the feasibility of the process. Thus, elemental phosphorus vapor was substituted for the PCl_3 vapor and the 600°C experiment ran again. Results indicated more gallium

phosphide synthesis and product, but still far too little to be satisfactory.

It was considered that the rate of attack of chlorine would increase with temperature, yet the synthesis rate might be even greater with increased temperature, and a re-cycling technique at higher temperatures could accomplish efficient conversion. In the interest of completely exploring this method, a revised apparatus was constructed, incorporating a 10-inch long reaction zone, capable of 1100°C operation. Experimental runs were carried out at 600°C, 800°C and 1075°C. The product quantity increased, but was too little to be practical as a synthesis process.

Gallium Triiodide and Phosphorus Method:

The vapor synthesis from gallium triiodide and elemental phosphorus was explored similarly to the trichloride. The gallium triiodide was prepared in the same manner, and gallium phosphide synthesis carried out at 600°C, 800°C and 1050°C. Results closely paralleled that of the chloride method; recovery quantity was very small in each case.

Effort in use of this specific vapor series has been suspended; other vapor techniques will be considered on their merits, and explored briefly when considered feasible.

D. Melt Growth*:

The gallium phosphide melt growth phase ran into serious difficulties early in this work period. These difficulties have been primarily due to a change from Alfrax insulating material in the furnace, to an improved graphite insulation. The old insulation had become saturated with vapor products and physically deteriorated to the degree that replacement was mandatory. It is worthy of note that temperatures in excess of 2000°C and pressures of 50 atmospheres for periods of hours are routine in this equipment.

Previous to the change of insulation, temperature calibration indicated a broad vertical gradient existed in the heater, peaking approximately at the center of the heater. Temperature is measured at this height by a graphite-graphite thermocouple located between the crucible and the heater walls. Thermocouple output is measured by a recorder, and has been correlated to power input with fairly good reproducibility.

Initial melt calibration with the new insulation agreed rather well with temperatures recorded and power input. However, first serious melt runs resulted in crucible failure, apparently due to excessive temperature. Runs with incrementally decreasing temperature immediately indicated melting was not accomplished below the temperature at which crucible failure had occurred.

Resolving this anomaly was a rather slow process. The study established the existence of a rather sharp temperature peak of the order of 200°C greater than that observed at the thermocouple location. The effect of the excessive temperatures are illustrated in Figure 6, where the tungsten carbide outer shield is observed to have softened and swelled at the base.

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* The work on this phase was performed by Lloyd W. Brown.

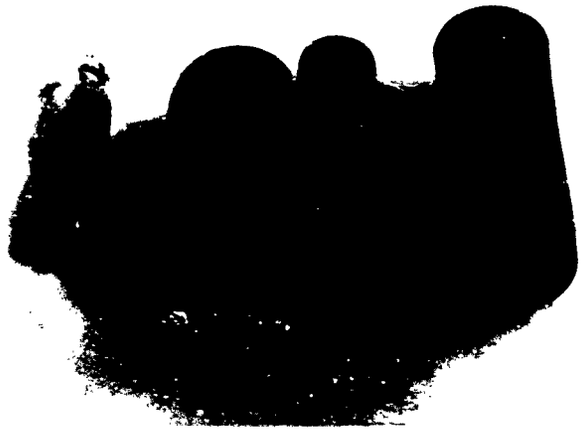

Figure 6. Melt Growth Crucible and Shield Assembly.

The net effect of this temperature differential was to produce either incomplete melting, or ingots in which cooling rates from the melt were so excessive that micro-granular structure resulted. It is of interest to note that these difficulties were not peculiar to the material. Similar effects were noted in the melt growth of cadmium sulfide crystals in a different in-house study.

Correction of this problem was accomplished by a change in thermocouple location and re-calibration runs on known melting point materials. Currently, melt growth has begun, with incremental temperature increases beginning at a temperature just below the melting point of gallium phosphide to establish the proper temperature and pull rates to obtain good crystal structure.

A total of sixteen melt runs and twenty calibration runs were carried out during this period. Of the melt runs, four produced usable material, eight were of micro-granular structure or unmelted, and four ruptured during furnacing and decomposed.

Indicating the acquisition of control, the last melt growth run produced a fully melted, transparent ingot of 4-grams weight, of good crystal structure. Strenuous effort is being exerted and the prognosis of rapid progress in this phase appears reasonable.

E. Epitaxy: Sealed Ampoule Iodine Transport*

Epitaxial growth of gallium phosphide on gallium arsenide substrates has been carried out by two methods. Method #1 is of the sealed ampoule type, using iodine as the transport vehicle. Typical apparatus is shown schematically in Figure 7. Source temperature was 1000°C, substrate temperature 750°C, and growth was carried out for periods of 30 minutes, 1 hour, and 2 hours. Results were very good. Layers of 8 to 60 microns thickness were observed and measured. Figure 8 illustrates the transparency of such a layer approximately 20 microns thick, when observed microscopically with the specimen illuminated from the side. Some polishing damage was observed at the interface in this specimen. This may be due to the differential hardness of the two materials, or may be the result of the small difference in unit cell dimensions producing dislocations along the interface. The effect of any such defects, if present, do not appear serious in preliminary device applications, as will be discussed later.

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* The work on this phase was performed by John C. Budiselic.

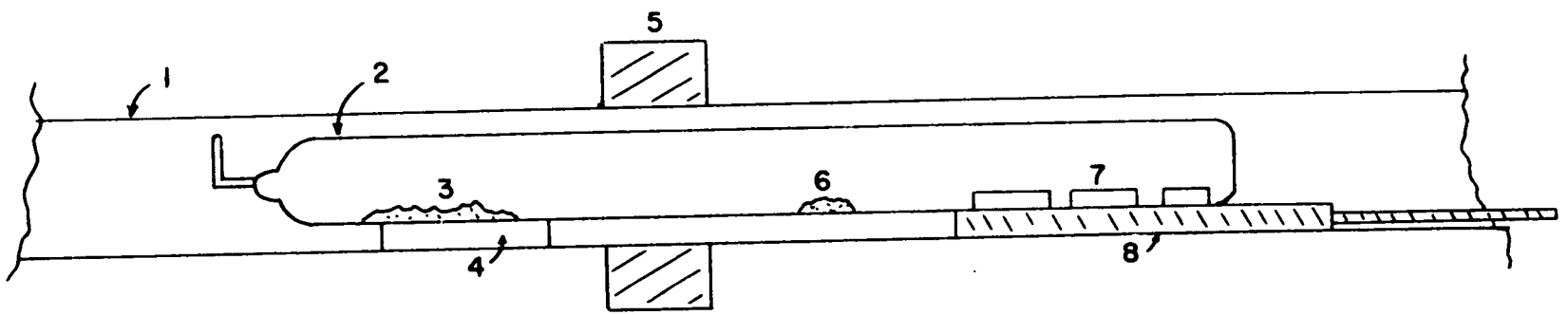

Figure 7 Iodine Transport Epitaxy System.

1. Quartz Tube
2. Sealed Ampoule
3. Gallium Phosphide Charge
4. Quartz Support
5. Insulating Ring
6. Iodine
7. Gallium Arsenide Wafers
8. Copper Heat Sink

Figure 8. Cross-Section Epitaxial Gallium Phosphide on Gallium Arsenide Substrate.

Surface conditions of such epitaxial layers were carefully observed in forty-nine specimens. Initially, attack and erosion of substrates with subsequent irregularities of the grown layer was observed. This was considered the result of early attack by the iodine vapor, aggravated by simultaneous heating of source and substrate. A technique was evolved whereby the iodine and source reaction was initiated first at 900°C, with the substrate temperature at approximately 500 degrees for a short period, preliminary to placement at the fixed, high temperature zones in furnacing.

Improved results were obtained, with recent surfaces remaining very smooth and highly reflective, changed only in color to a grey appearance.

Initial growth incorporated no dopant, layers grown thus generally indicated n-type conductivity when tested by the thermal method. Surface resistivity of initial substrates, high polished chemically, and epitaxial layers on the respective substrate, is essentially the same. Table VII indicates this similarity, and also the calculated net carrier concentration.

TABLE VII

Surface Resistivity and Carrier Concentration for Substrate and GaP Epitaxial Layers.

Identity	Epitaxial Layer - Microns	Surface Resistivity Ohms/Square	Carrier Concentration Atoms/cc
GaAs Control,	0	10^4	1×10^{16}
EG-28,	25	1×10^5	1×10^{16}
EG-30,	20	2×10^5	5×10^{15}
EG-34	9	5×10^4	2×10^{16}
EG-39	10	1×10^5	1×10^{16}
EG-46	10	1×10^5	1×10^{16}

Calculation of net carrier concentration is based on the formula -

$$P = \frac{1}{N_c\ (e)\ (u)} \qquad (1)$$

where

P = resistivity ohm-cm
e = electron charge 1.6×10^{-19} volts
and u = electron or hole mobility.

The measurement of surface (sheet) resistance by two probe methods, of highly polished surfaces incurs error due to contact resistance, etc , and must be considered approximations especially where such surfaces are not highly doped, i.e., high orders of resistance.

It should be noted that the mobility of gallium phosphide reported in the literature is approximately an order of magnitude lower than gallium arsenide. Thus, similar surface resistance measurements of the two implies an approximate order of magnitude increase in gallium phosphide net carrier concentrations.

Stated differently, for a given similar carrier concentration, an order of magnitude greater surface resistance would be expected. General agreement with this principle has been observed in these measurements.

Epitaxial growth of p-type gallium phosphide layers on n-type gallium arsenide substrates was carried out similarly, using a few milligrams of zinc iodide as both the transport vehicle and dopant. Layers of 10 to 50 microns thickness were grown. Typing by thermal methods indicated consistently p-type conductivity. Surface resistances ranged in the order of 10^4 ohms per square indicating carrier concentration of the order of 10^{17} atoms per cm^3. Significant diode and photo parameters were observed in these structures and are described subsequently.

F. Open-Flow Iodine Epitaxy:

The use of an open-flow system was considered desirable and feasible, and offered significant advantages where growth of alternate conductivity type layers with abrupt transition were desired. The system is diagrammed in Figure 9. Elemental iodine, vaporized by a constant temperature water bath is carried by hydrogen gas over a source/charge of gallium phosphide at 1000°C where reaction occurs. The reaction products migrate gently down a temperature gradient and pass over the 750°C gallium arsenide substrates, disproportionating and growing epitaxially on the substrates. By-products are exhausted through suitable traps.

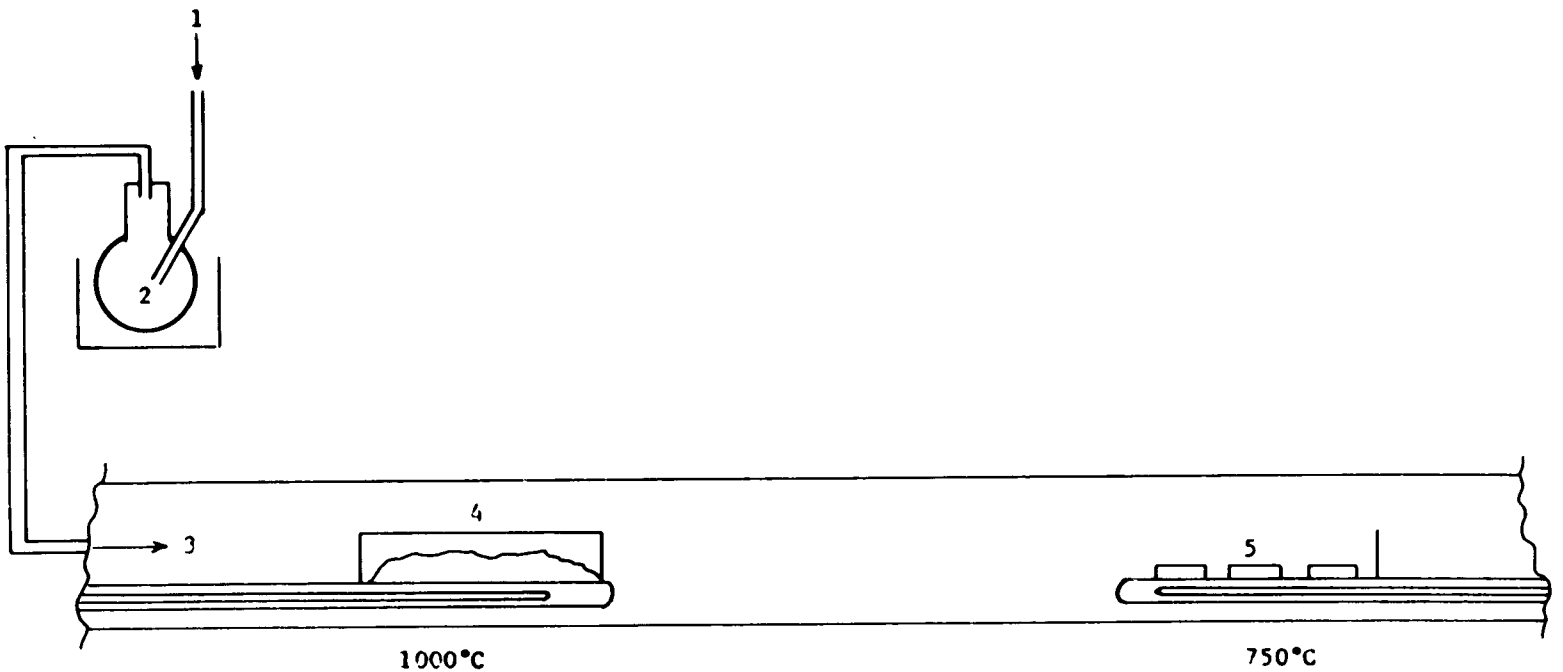

Figure 9. Open-Flow Gallium Phosphide Epitaxy System.

1. Argon Inlet
2. Iodine Boiler
3. Iodine Inlet
4. Gallium Phosphide Source
5. Gallium Arsenide Substrate.

The gallium phosphide source, contained in a boat, is arranged to allow insertion and/or removal from the 1000°C zone, as is also the substrate platform. After purging, an atmosphere of hydrogen is established, the substrates inserted for in-situ cleaning. The iodine flow and insertion of source is begun simultaneously, and growth carried out for the prescribed time. The source is removed to a cool portion of the tube, iodine flow terminated and hydrogen used to sweep out residual vapor products. (At this point a gallium phosphide charge/source of opposite conductivity type doping may be inserted and continued growth carried out without distrubing the system integrity, and with minimum time between growth).

Undoped layers of 10 to 25 microns thickness were successfully grown using this system. Results in each case were equal, or superior, to the sealed ampoule method, and eliminate sealing and pumping operations with consequent saving of time and materials. Surfaces were excellent; uniform in thickness and very smooth. The requirements for reverse growth, i.e., gallium arsenide on gallium phosphide substrates, are less stringent, and exploratory runs indicate this system is excellently suitable for it. Discussion of this application will be made subsequently under "Device Fabrication".

G. Gallium Phosphide Material Evaluation:

Electronic.

The evaluation of the electronic parameters has been inhibited for lack of large single crystal specimens. Specimens obtained from melt growth ingot #M-9, with possible grain boundaries, were measured as indicated below:

Specimen: M6303-DR Ingot M-9
Resistivity: 2×10^3 ohm-cm
Net Carrier Concentration: 10^{14} atoms/cm.^{3}

It is considered probable that grain boundaries do exist in this specimen and the indicated resistivity is higher than actual. Other specimens are in process and will allow more exact determination.

Visible Spectrum.

Since one device application of this material will involve signal transmission in the form of light, optical transmission data are of interest. Two specimens were selected, polished and measured. A Bausch & Lomb Spectrophotometer was used, with resolution of 100 A°. Subsequently the same specimens were measured with a Beckman DU instrument, with resolution of 5 A°. Excellent agreement was obtained, particularly in the band edge region. Figure 10 illustrates the transmission data. Specimen M6306-AZ, approximately 1-mm thick, from melt grown ingot #M-10, was a cross section slice. Specimen M6306-BA, 3.0-mm thick, was a cross section slice of a vapor grown plate.

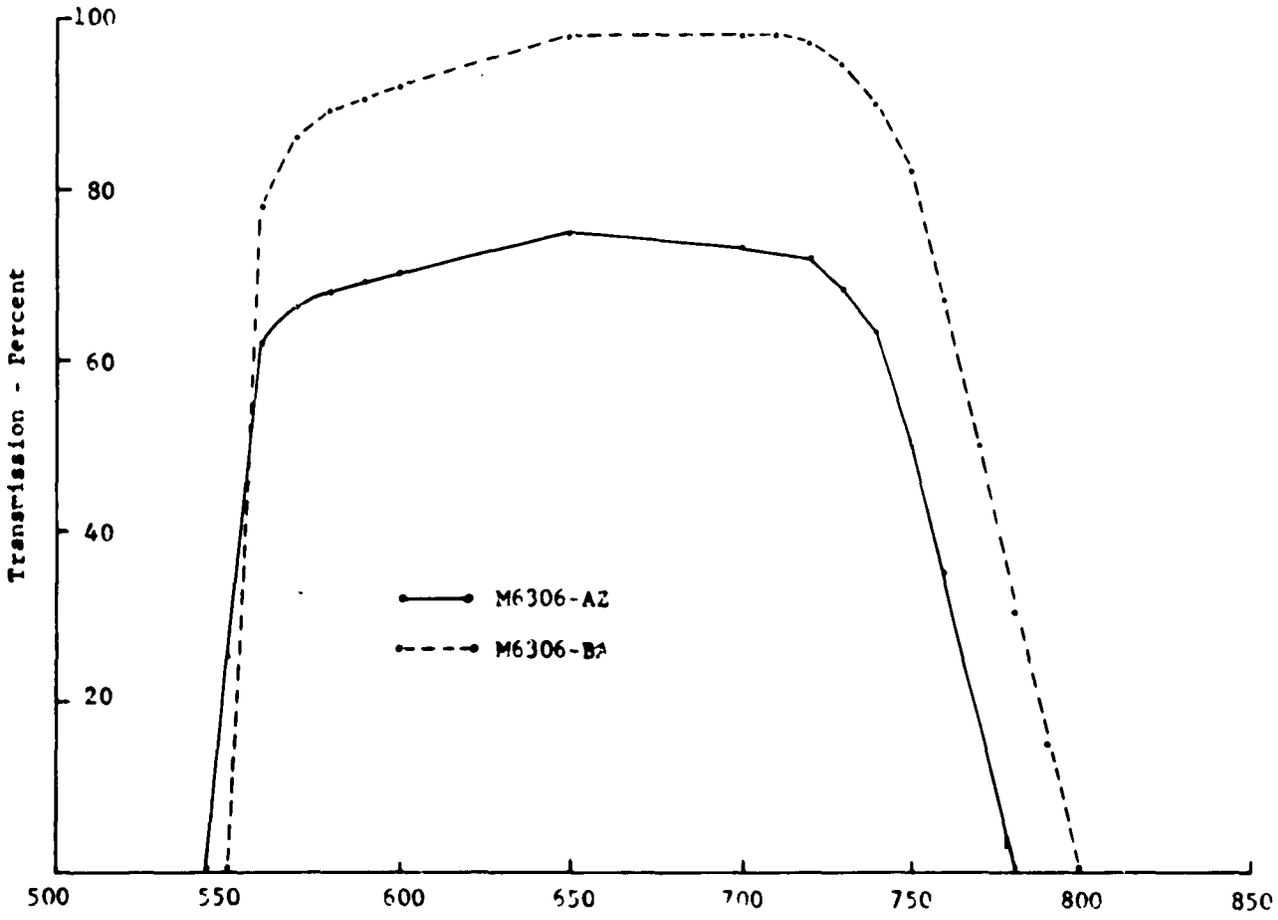

Figure 10. Absolute Transmission of Gallium Phosphide Specimens.

Referring to Figure 10, the transmission of the vapor phase, 3-mm Specimen M6306-BA is noted to be higher numerically, than the thinner melt grown specimen - M6306-AZ. This effect may be real, but is dependent upon the spectral reflectance of the specimen and therefore depends upon the polish and flatness of its surface. In the absence of reflectance measurements, the numerical difference is considered the result of degree of polish. Of importance is the indication that either material, of n-type conductivity, transmits the visible spectrum above 550 millimicrons with very little loss if allowance is made for scattering and reflectance at the surfaces. Transmission/absorbance of p-type specimens is planned.

Infrared Spectrum.

The infrared transmission for the same specimens was measured using a Beckman Dual Beam Infrared Spectrophotometer. Figure 11 illustrates the absolute transmission of both specimens. In this case it is observed the transmission of the thicker specimen is significantly less than the thinner specimen, #M6306-AZ, although numerically small in both cases. This was expected since specimen thickness is much greater than ideal.

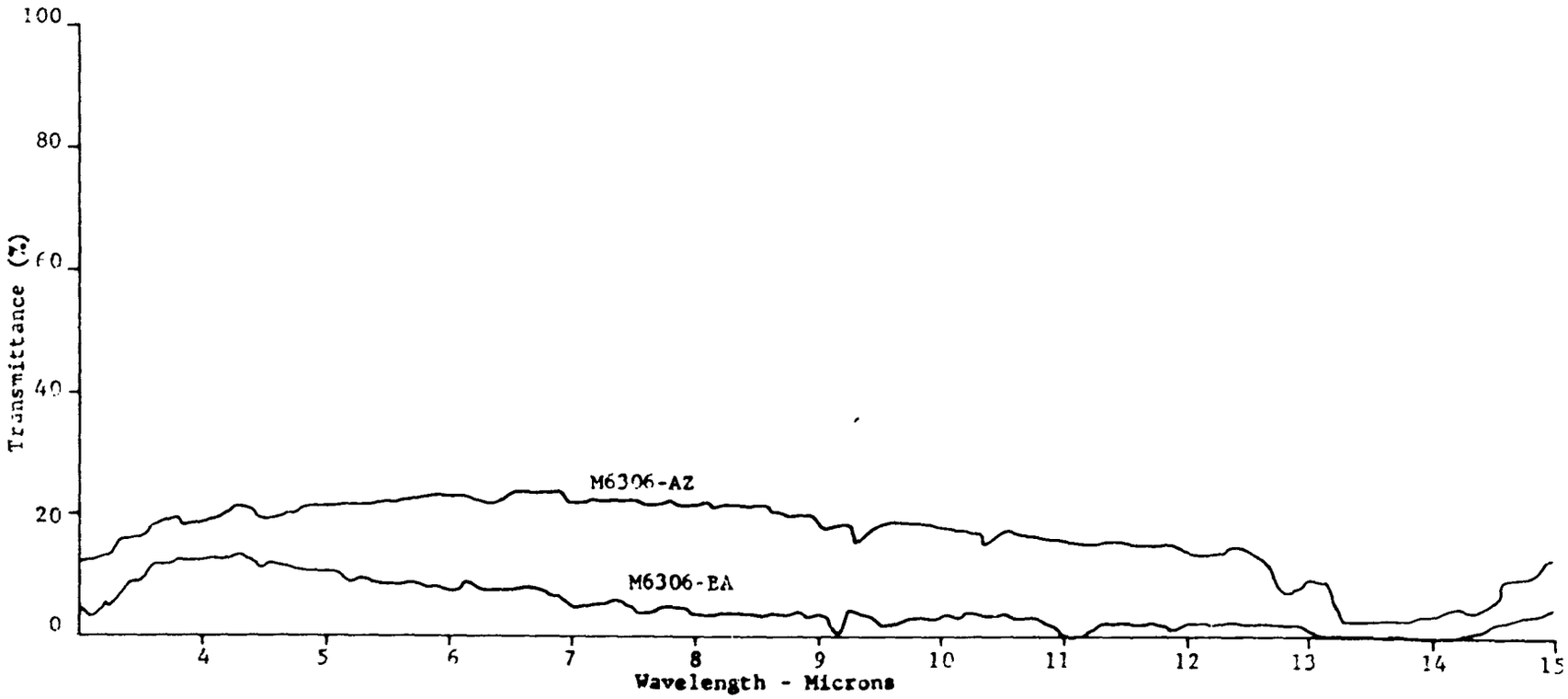

Figure 11. Infrared Transmission of Gallium Phosphide Specimens

H. Device Fabrication:

Diodes of both diffused and alloyed structure were fabricated. Pertinent data is detailed below for the zinc diffused gallium phosphide diodes fabricated thus far.

Bulk GaP Resistivity = 2 x 10^3 ohm-cm (M-9)
Bulk GaP Carrier Concentration = 10^{15} atoms/cm^3
Final Surface Preparation = Chemically polished methyl alcohol + chlorine.
Zinc Diffusion = 800°C- 15 Min. Sealed ampoule.
Bottom (n) Contact = In, Sb, Sn Alloy.
Top (p) Contact = Pb-Cd Alloy.

The diode characteristics of these diodes, made by Tektronix #575 Curve Tracer, are illustrated in Figure 12. The characteristic indicates considerable resistance in forward slope, and is considered the effect of the undoped high resistivity bulk material. The diode results reported here are tentative, and will be more precise and informative when doped single crystal material is available.

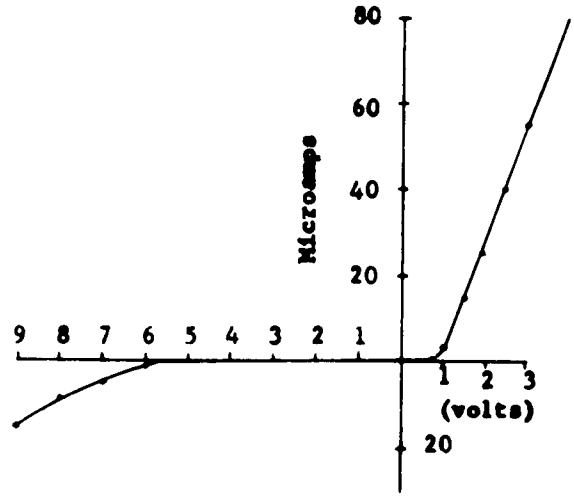

Figure 12. Gallium Phosphide Diffused Diode Characteristics.

Alloyed Diodes.

Alloyed diodes were fabricated from bulk gallium phosphide ingot #M-10. This ingot was of somewhat lower bulk resistivity than that used for the diffused diodes. Pertinent data are tabulated below:

Bulk Resistivity = 7×10^2 ohm-cm (M-10)
Bulk GaP carrier concentration = 10^{16} atoms/cc.
Final Surface Preparation = Chemically polished methyl alcohol + chlorine.
Alloyed Junction/Contact = In-Au-Zn alloy.
Bottom Contact = Electroplated nickel, solder coated.

Diode characteristics were measured by a Tektronix #575 Curve Tracer Oscilloscope, and are diagrammed in Figure 13.

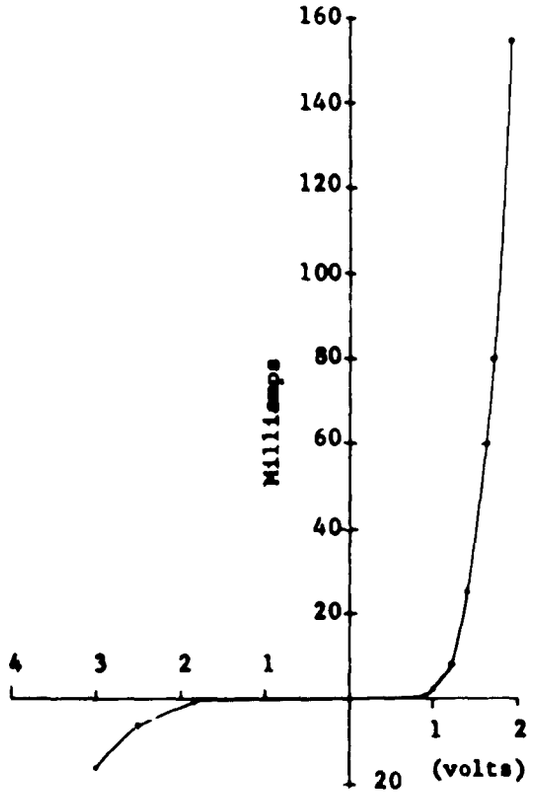

Figure 13. Alloyed Gallium Phosphide Diode Characteristics.

Epitaxial Diodes.

Epitaxial growth of p-type gallium phosphide on n-type gallium arsenide substrates was carried out to explore the possible difficulties or peculiarities in junctions where the possibility,or even probability, of self-diffusion exists. Epitaxy was done by the sealed ampoule, zinc iodide transport method previously described. Two milligrams zinc iodide were used, producing low order doping.

Surface resistivity by 2-probe methods indicated zinc carrier concentration to be approximately 10^{16} to 10^{17} atoms/cm^3. Contact to both "p" and "n" surfaces was made with electroplated nickle and solder coating. Mesas were etched and individual diodes scribed, separated and mounted on TO-5 transistor mounts. Typical data for these diodes are illustrated in Figure 14.

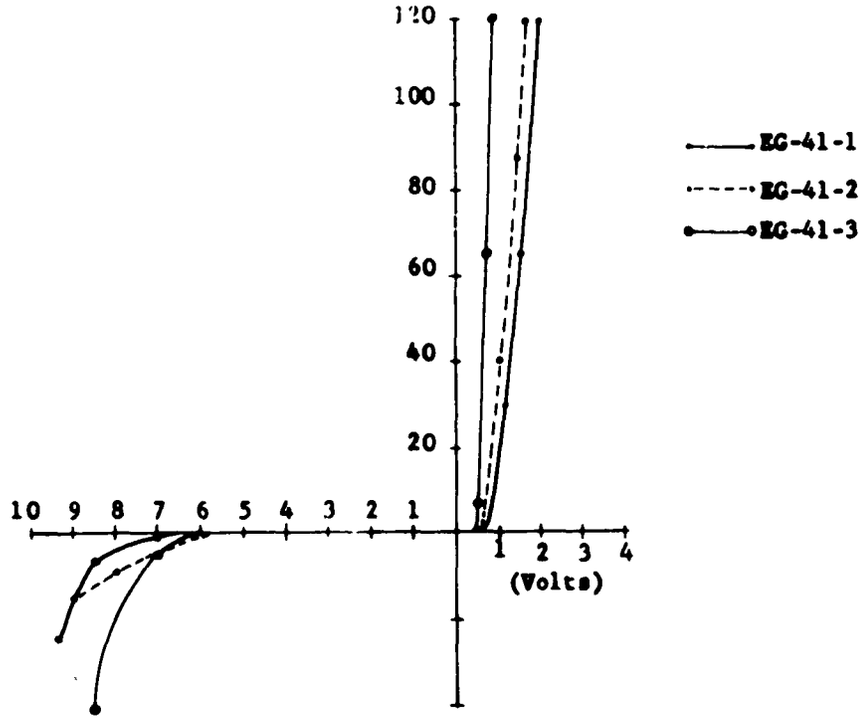

Figure 14. Diode Characteristics of Epitaxial Gallium Phosphide on Gallium Arsenide Diodes.

I. Device Evaluation:

Device fabrication studies have just begun; thus the evaluation results given here are tentative and of an indicative nature. The diode response for diffused junction gallium phosphide devices (Fig.12) indicate considerable forward resistive effects. This series "R" may be composed of bulk resistance, contact resistance, sheet resistance in the diffused layer, and/or grain boundary barriers. Surface (sheet resistance) measurements indicate fairly high values, which implies low carrier concentrations to be one of the principal factors. Bulk resistivity of material is also considered a contributing factor, since the material was not doped in growth. Low resistivity, doped material presumably will be available soon for diode fabrication.

The alloyed diodes (Fig.13) indicate better characteristics, and to a degree corroborate the above contention. Lower bulk resistivity material was used; the alloy re-grown junction gave significantly higher p-type conduction. Resultant diode curves have much steeper forward slope.

The epitaxial gallium phosphide diodes (Fig.14) were grown using two milligrams of zinc iodide, now considered less than should be used for adequate doping. Some resistive slope is observed in these diodes; bulk resistance and low doping levels are considered responsible. The layers were grown for epitaxial studies per se; subsequent layers will be heavily doped for device applications. Some insight into doping concentrations can be obtained from a plot of ln I versus V of a diode. The slope, d(qv/kt)/d ln I of a conventional, heavily doped semiconductor junction in the straight line portion, has a value of 2.0 or more. Plots were made of several of the epitaxial gallium phosphide on gallium arsenide diodes. Typical of these is Figure 15.

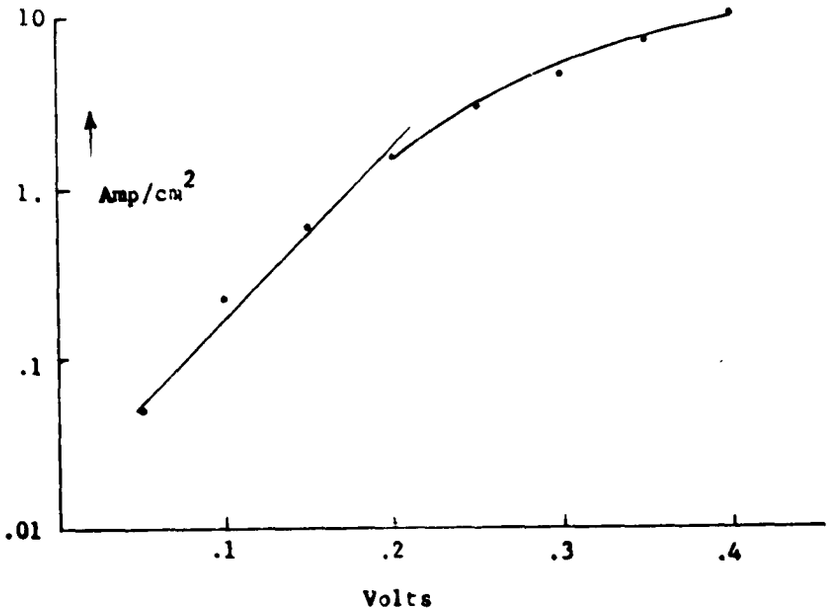

Figure 15. Plot ln I versus V of Epitaxial Gallium Phosphide Diodes.

The slope indicated was between 1.0 and 1.5 for several such diodes. The inference is of a graded junction, or one in which the doping gradient is not abrupt. It is expected that this slope will be increased significantly with increased acceptor doping during growth. Cognizance is taken of an alternative, e.g., heterojunction rectification, where only a simple barrier lowering mechanism is involved. This alternative appears unlikely, since definite type change was observed by thermal typing.

Photovoltaic measurements were made of several epitaxial "p" gallium phosphide on "n" gallium arsenide wafers, previous to mesa etching. The object here was to ascertain, if possible, to what degree diffusion of zinc carriers into the gallium arsenide substrate was occurring. Due to the

difference in band gap, it is considered that a V_{oc} in excess of 1.0 volt might be observed where a good p-n junction is made in gallium phosphide. This value is considerably more than a similar gallium arsenide junction might produce. Also, in the first case, a significant increase in spectral response in the blue region might be observed.

V_{oc} was measured with a plated contact on the bottom of each specimen, and a point probe to the surface. Maximum V_{oc} measured is listed for each type of device.

Zinc Diffused Gallium Phosphide Diodes	= 0.76 V_{oc}
Alloyed Gallium Phosphide Diodes	= 0.68 "
Epitaxial GaP on GaAs Diodes	= 0.78 "

These photovoltages, although less than expected, still are fairly high and are encouraging with regard to material properties. I_{sc}/cm^2 values of the order of 5 ma/cm^2 to a probe were observed. The foregoing data could be made without disrupting the mesa-diode processing or special fabrication steps. More precise evaluation of photo-parameters is contemplated as the device phase progresses.

Reference has been made to the possibility of diffusion of zinc into the gallium arsenide substrate, during the growth of the zinc doped gallium phosphide layer. The growth period, temperature of 750°C and zinc environment establishes the conditions necessary for diffusion. Thus in the "p" gallium phosphide on "n" gallium arsenide, the junction may lie within the substrate rather than at the interface. It is considered feasible to evaluate the junction position at least qualitatively by spectral response, since the gallium phosphide response should be measurably greater in the blue wavelengths.

Spectral response data were made of an epitaxial "p" gallium phosphide on gallium arsenide wafer, Figure 16.

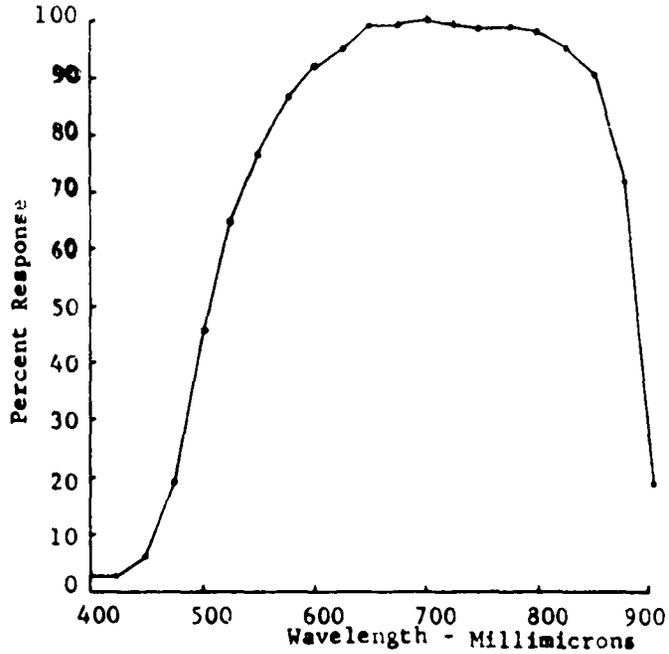

Figure 16. Spectral Response of "p" Gallium Phosphide on Gallium Arsenide Substrate. EG-35-2.

The response indicated is similar to that of a gallium arsenide diode with a shallow junction. The lack of significant response in the 0.4 micron range could be the result of the deep (10 micron thickness of gallium phosphide layer) junction. From Figure 10, one observes high absorption of this wavelength; short lifetime and poor collection of carriers could thus be invoked to explain the low response. However, it is considered the spectral response supports the probability of self-diffusion during the epitaxial growth of "p" type gallium phosphide on gallium arsenide.

The foregoing implies difficulty in realizing a junction within the epitaxial gallium phosphide growth. Various alternates are available, such as n-type gallium phosphide on n-type gallium arsenide with subsequent diffusion or alloying of a junction. The most attractive of these is the

epitaxial growth of p-type gallium arsenide simultaneously on both sides of an n-type gallium phosphide substrate. This configuration offers assurance of junction location at the interface or within the gallium phosphide, reduces heat cycles to the minimums of both time and temperature and can be readily accomplished with the same iodine transport technique. Thus initial exploration is intended along these lines.

V. SUMMARY

The synthesis of gallium phosphide has been pursued, with improvements in technique, product quality and efficiency. Several alternate vapor synthesis methods were explored with negative results from a practical viewpoint.

The melt growth of gallium phosphide was impeded by furnacing difficulties which essentially have now been resolved. Improved insulation is expected to enhance growth of single crystal material.

Epitaxial growth of gallium phosphide has been accomplished with good control of growth rates and doping by the sealed ampoule iodine transport method. Photographic evidence of structures indicate excellent quality. X-ray identity of single crystal structure has been made.

Epitaxial growth of gallium phosphide by an open-flow iodine transport system has been accomplished. Results are equally good and this method offers facilities in alternate type, consecutive growth of layers without interruption.

Optical transmission of bulk undoped gallium phosphide material has been determined with a high degree of accuracy. Transmission in the visible spectrum is very good, and supports the feasibility of light operated 3-terminal devices.

Infrared transmission of two samples was determined. Transmission was low between 3 and 16 microns. Samples were not single crystal material, and better transmission with less scattering may be expected from single crystal specimens.

Diffused diodes were fabricated and tested. Resistive effects were noted and considered the result of bulk resistivity and low mobility of starting material. Improved results are anticipated with lower resistivity material now being prepared.

Alloyed diodes were prepared and tested. Rather good forward characteristics were observed.

Epitaxial diodes were fabricated by growth of p-type gallium phosphide layers on n-type gallium arsenide substrates. Diode characteristics were rather good in both forward and reverse direction. Log I versus V plots of these diodes give "n" values of 1.0 to 1.5, which does not fit the principle of highly doped semiconductor junctions. Tentatively, it is considered probable the low net "n" carrier concentration in the bulk material is responsible.

VI. FUTURE STUDIES

Future studies are planned to accomplish the following:

Further improvement in the synthesis of bulk gallium phosphide.

Growth of single crystal ingots of gallium phosphide, undoped, and doped "p" and "n" type ingots. This is the principal goal and effort. Both melt growth and vapor phase growth are considered.

Evaluation of the single crystal materials in terms of crystal structure, resistivity, mobility, optical transmission, etc.

Direct junction formation by diffusion and alloying techniques and evaluation of such junctions in terms of barrier heights, junction capacitance and temperature characteristics.

Epitaxially grown junctions of two and three terminal geometries and evaluation in terms of diode characteristics and transfer characteristics. Particular emphasis is to be on electroluminescence and optical transfer characteristics of the 3-terminal geometry.

VII. REFERENCE

1. First Quarterly Technical Report, "Gallium Phosphide Devices:, April 14, 1963. Contract Nr. DA-36-039-AMC-00103(E). The Eagle-Picher Company.

VIII. PERSONNEL

Engineering Time Expended from March 14, 1963 to June 14, 1963, inclusive.

Ames, William A., ...	8	Hours
Brown, Lloyd W. Brown,.	225	"
Budiselic, John C., ...	336	"
Olds, Larry Lee,.	12	"
Powderly, Joseph E.,.	23	"
Roderique, J. S., ...	288	"
Starks, Ralph J., ...	80	"
Stone, Louis E.,.	128	"
Webb, George N.,.	40	"
Total ,	1,140	Hours.

AD_____ Accessories No.____ UNCLASSIFIED

The Eagle-Picher Company, Chemical & Metals Division, Miami, Oklahoma.
GALLIUM PHOSPHIDE DEVICES
L. E. Stone, J. R. Musgrave.

Second Quarterly Technical Report - March 14, 1963 to June 14, 1963.
42 pp - Illustrations, Graphs.

Gallium phosphide synthesis, melt growth; GaP Epitaxy on GaAs; GaP devices and Data; Description Techniques and Apparatus.

1. Gallium Phosphide
2. GaP Epitaxy
3. GaP Devices

4. Contract Nr. DA-36-039-AMC-00103(E).

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