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THIRD QUARTERLY TECHNICAL REPORT

Report Date: February 28, 1963
November 1, 1962 to February 1, 1963

"VARIABLE ENERGY GAP DEVICE"

CONTRACT NR. DA-36-039-SC-89106

Placed By:

*U. S. Army Signal Research & Development
Laboratories, Fort Monmouth, New Jersey*



THE EAGLE-PICHER COMPANY

Chemicals & Metals Division,

Research Laboratories,

Miami, Oklahoma

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THIRD QUARTERLY TECHNICAL REPORT
Covering the Period -
November 1, 1962 to February 1, 1963.

"VARIABLE ENERGY GAP DEVICES"

Order No. 1208-PM-62-93-93 (4912)
Date of Contract: May 1, 1962.
Amount of Contract: \$34,791.00
Contract Number: DA-36-039-SC-89106

Report Prepared By:

L. E. Stone
Geo. N. Webb

Edited By:

J. R. Musgrave

The Eagle-Picher Company,
Research Laboratories,
Miami, Oklahoma.

The work performed under this Contract was made possible by the support of The United States Signal Research and Development Agency, Fort Monmouth, New Jersey.

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I. PURPOSE

The objective of this investigation is to evaluate the variable band gap structure $\text{GaAs}_x\text{-GaP}_{1-x}$, with a gallium phosphide surface concentration approaching 100 percent, decreasing in concentration to zero at some discrete depth, and containing a single p-n junction. The photovoltaic cell was considered the best device form for evaluation and has been the principal device form until very recently. The determination of optimums of diffusion, resistivity, doping, minimizing junction depths, optimizing contact ohmicity, reducing sheet resistivity, maintaining highest lifetime, etc., have been the chief practical goals. Evaluation of the appropriate electronic and optical parameters was planned and carried out, to define any advantageous characteristics in spectral response, temperature performance, carrier injection, etc. Since some evidence has been observed of improved characteristics, but the photovoltaic device is uniquely vulnerable to impurity contamination due to the shallow junctions involved, it was considered feasible that the inherent advantages of the materials and structure might be more definitely demonstrable in other device forms. A Conference at Evans Laboratory, Fort Monmouth, N.J., on February 13, 1963 resulted in mutual agreement to explore a three terminal device using the same materials systems. The device investigation would be aimed toward carrier injection improvement. The fabrication of such a device is within our capabilities, and would exploit all of the technology accumulated in the earlier investigations of this structure and materials system.

II. ABSTRACT

Compensation effects and "scatter" in device fabrication was traced to phosphorus impurities during phosphorus diffusion/conversion. Phosphorus purification was begun in parallel with batch selection search for high purity material. In-house purification was halted when high purity phosphorus was obtained. Induction heating (30 mc) of wafers for diffusion of shallow junctions was carried out with some success. Spectral response of selected devices were found to be very broad. Principal difficulty observed was exhaustion of zinc vapor by condensation on the cool walls of the diffusion chamber.

Epitaxial growth of GaP on GaAs was carried out by two methods. Growth by iodine transport appears better than growth closely adjacent to GaP synthesis zone. Laue back reflection technique indicates single crystal structure of both types of epitaxial layers. GaP melt runs were successful in producing bulk material as source of epitaxy.

Improved technique and facilities in chemically polishing GaAs surfaces have been established.

Literature search and initial steps toward fabrication of 3-terminal devices begun.

III. PUBLICATIONS, CONFERENCES & REPORTS

Conferences:

A conference was held at Fort Monmouth, Evans Laboratories, on February 13, 1963. Present were Messrs. Robert Yatsko, Philip Newman, and James Kesperis, of Evans Laboratories, and Mr. Louis E. Stone, of Eagle-Picher Company. The subject of the conference was the possible choice of an alternate device geometry to yield more definite determination of the theoretical advantages of this materials system. By mutual agreement, as a result of careful discussion, a device was decided upon. The proposed device would be of a 3-terminal nature. Principal practical goal would be to show by device transfer characteristics an improvement in carrier injection efficiency. The conference was informative and very useful.

Reports:

Monthly Letter-Type Reports #8 and #9 were submitted on schedule.

IV. FACTUAL DATA

A. INTRODUCTION:

Progress in fabrication of variable gap structures arrived at the stage where compensation effects of phosphorus impurities were limiting further progress and producing scatter in data. This compensation was also grading the junctions and making difficult, if not impossible, the object of achieving a junction in the upper portions of the GaP structure. Thus, effort in this work period was aimed at eliminating such impurities and improvement in diffusion techniques toward high temperature, short time diffusion to achieve shallow high carrier density junctions.

Parallel studies to obtain melt grown GaP ingots as source material for epitaxial growth of GaP layers on GaAs were carried out. Some success was obtained in each category.

Improvement in chemical polishing techniques were made and described herein.

B. Phosphorus Purity.

Previous studies indicated that diffusion of phosphorus produced a GaP layer which was compensated to some degree. In extreme cases, especially in the long time high pressure diffusions, type conversion to p-type occurred. Even in short time diffusions the effect of partial compensation could be observed and produced scatter in device parameters. A secondary effect was noted in that the finished junction was graded to some degree, rather than being abrupt as desired. Spectrographic analyses of semiconductor grade phosphorus indicated wide variations in impurity levels from

batch to batch obtained from the same company. Phosphorus obtained from a second source also indicated unsatisfactory levels of impurities. Table I illustrates typical values in parts per million.

TABLE I

Spectrographic Analysis of Phosphorus Lots - Parts Per Million.

<u>Sample</u>	<u>Source</u>	<u>Mg</u>	<u>Pb</u>	<u>Si</u>	<u>Fe</u>	<u>Al</u>	<u>Cu</u>	<u>Ca</u>	<u>Others</u>
M6207 BQ	A	5	1	40	1	5	1	1	-
M6212 BW	A	20	2	100	10	10	2	50	32
M6212 AP	B	20	3	100	5	5	2	10	36

An effort was made to purify the phosphorus by sublimation. Sublimation was carried out under vacuum conditions in quartz, and condensed at a cool zone; also by passing the phosphorus vapor through a heated, fused silica jet and condensed at a cold zone. Samples of starting material (M6212 AP) and the sublimed material (M6212 BM) were submitted for spectrographic analysis. The phosphorus (M6212 BM) sublimed through a heated jet was higher in impurity levels than that sublimed without passing through the hot zone. Both were significantly higher than the starting material, as indicated in Table II.

TABLE II

Spectrographic Analysis Before and After Sublimation.

	<u>Parts Per Million</u>							
	<u>Mg</u>	<u>Pb</u>	<u>Si</u>	<u>Fe</u>	<u>Al</u>	<u>Cu</u>	<u>Ca</u>	<u>Others</u>
M6212 AP (Before),	20	3	100	5	5	2	10	36
M6212 BM (After),	100	400	5%	1000	5000	50	2%	180

Further effort at sublimation in stainless steel had been planned. However, in parallel with in-house efforts, a program of selective "batch"

sampling was made from the commercial source "A". Several lots were obtained at this point, which were of extremely good quality, as indicated in Table III. The values in parts per million, are essentially the spectrographic limits of detection. With the acquisition of this material further in-house purification efforts were halted.

TABLE III

Spectrographic Analysis of New Lots of Phosphorus.

	Parts			Per			Million	
	Mg	Pb	Si	Fe	Al	Cu	Ca	Others
M6302 AA	< 0.5	----	< 5.0	< 1.0	< 2.0	< 0.5	< 0.5	-
M6301 CB	< 0.5	----	< 2.0	---	< 1.0	---	< 0.5	-

C. Diffusion by Induction Heating.

The importance of creating a very shallow (less than 1-micron) junction, having very high density of zinc carriers, was emphasized by the imposed limitation that no etching procedures be used to optimize performance of the photovoltaic device. The studies made of zinc diffusion indicate temperatures of the order of 800°C, coupled with short, precise diffusion time, would be productive. A disadvantage of conventional furnacing techniques is the significant time required for the specimen to reach furnace temperature, and the cooling effect on the furnace of inserting a cold boat, specimen and dopant therein. Additionally, conventional furnacing produces an environment wherein the specimen is cooler than the surroundings, encouraging the diffusion of contaminants in it.

The use of induction heating appeared attractive, providing direct coupling into specimens, without the use of a susceptor such as graphite,

could be achieved. The geometry of the necessary work coil predicated frequencies of the order of 30 megacycles as necessary to achieve an acceptable heating efficiency. An induction heater of this frequency range was acquired. Figure 1 illustrates the generator, front view, and Figure 2, the side view. Figure 3 illustrates the work coil, boat and substrates, preparatory to diffusion. Figure 4 indicates the appearance of boat, etc., subsequent to diffusion. Hydrogen gas atmosphere is used. GaAs was made to suscept directly, and the direct heating does produce several distinct advantages. The substrate can be raised easily to over 800°C in a matter of ten seconds; the quartz walls and boat, except in direct contact with the specimen (or a conductor) remains cool. One disadvantage observed was that rectangular specimens tend to heat unevenly, being significantly higher in temperature at the edges. This was conveniently eliminated by the use of a graphite button support for the specimen. The graphite button was baked out at 1200°C for 30 minutes before use. Original plans were to use an organic zinc compound (Di-methyl Zinc) as a source of dopant, decomposing it at the hot substrate. This proved hazardous and an alternate zinc source necessary. Two methods were used, both acceptable, but not entirely satisfactory. Zinc was vaporized from the surface of a graphite susceptor, upstream from the substrate. Figure 4 illustrates zinc diffused from a previously prepared GaAs-zinc alloy. These methods provide an acceptable, but not ideal, uniform vapor concentrations at the specimen. Several very good diffusion runs were made using this technique. Temperatures used were 750°C to 800°C, for periods of two to five minutes. The time interval is quite sharply defined by the rapid heating and cooling characteristics.

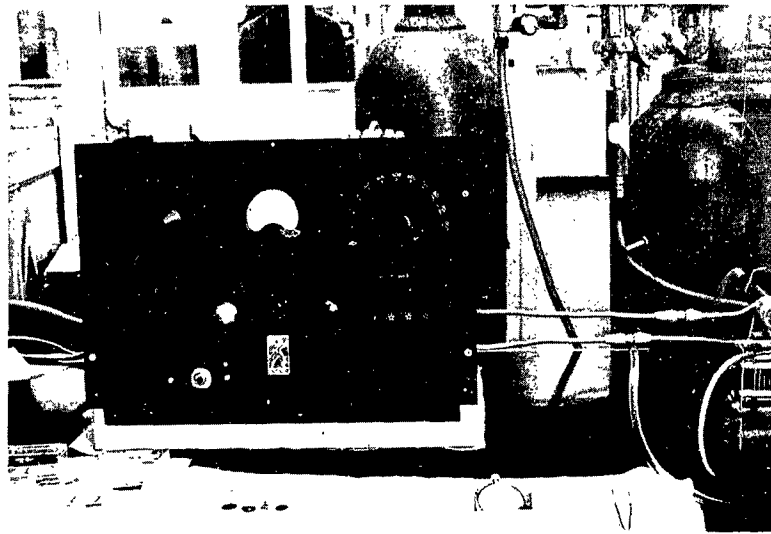


Figure 1. High Frequency Induction Heater. (Front View).

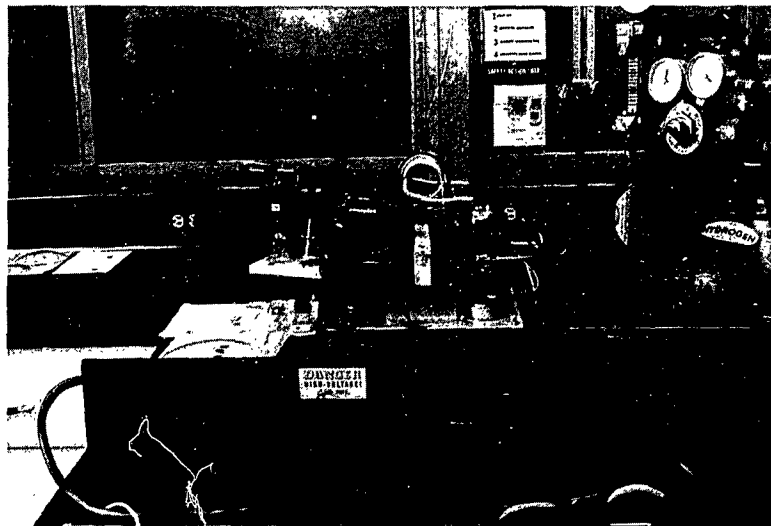


Figure 2. High Frequency Induction Heater, (Side View).

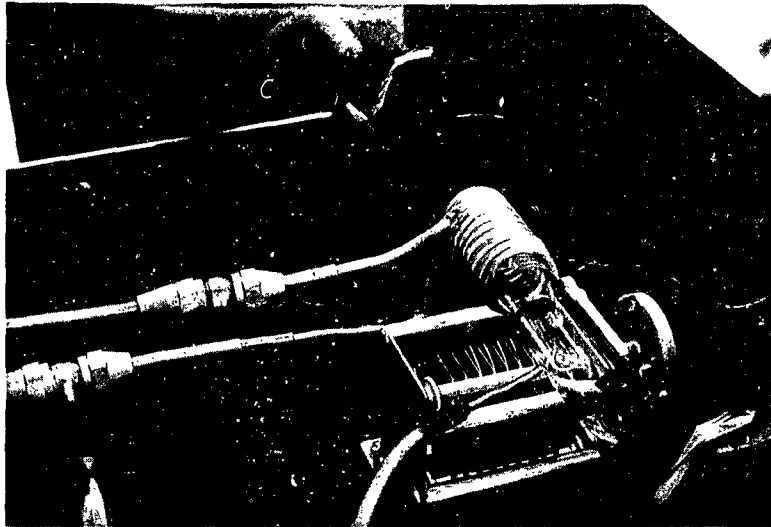


Figure 3. High Frequency Work Coil, Boat and Substrate Before Diffusion.

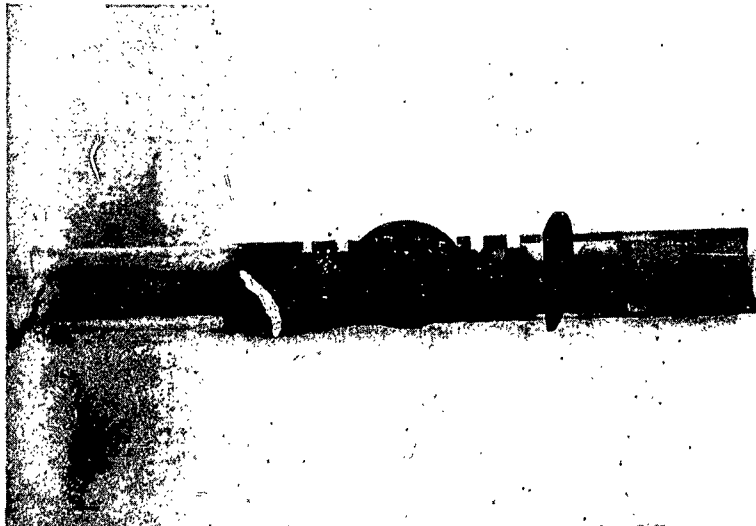


Figure 4. Boat and Substrate After Diffusion.

D. Epitaxial Growth Studies.

Two methods of epitaxial growth have been explored briefly. The first method incorporates the same general system used in synthesizing the GaP, i.e., Ga_2O_3 at a temperature of the order of 900°C , with phosphorus vapor passed over it, using hydrogen as a carrier gas. (Some mention of this method was made in the Second Technical Summary Report⁽¹⁾). The substrate was placed closely adjacent to the synthesis zone, and its temperature established, by means of a heat sink, at a value 50 degrees cooler than the synthesis zone. Figure 5 illustrates the essential components of the system. Experiments were carried out under similar conditions, with similar temperature gradients as indicated in Table IV.

TABLE IV

Epitaxy GaP on GaAs using Ga_2O_3 - Phosphorus Vapor.

<u>Group Numbers</u>	<u>Temp. °C Ga_2O_3</u>	<u>Temp. °C Substrate</u>	<u>Time Minutes</u>	<u>X-Ray & Optical Analysis</u>
1	950°C	910°C	120	Good Growth
2	800°C	765°C	120	No growth.

Laue x-ray patterns made on specimens of Group #1 indicate the growth to be single crystal in structure, as illustrated in Figure 6. The surface of the wafer was lightly textured in appearance by optical microscopy, and semi-transparent. Observed under polarized light, any surface damage revealed a characteristic orange color. Specimens of Group #2, by optical microscopy exhibited only scattered, tiny, nucleated crystals and etched chemically much the same as a control blank of GaAs only. The surfaces of Group #2 were covered by an encrusted Ga_2O_3 and GaP powder layer, which removed easily. These factors imply that this system requires temperatures above 850°C , a higher temperature than other techniques.

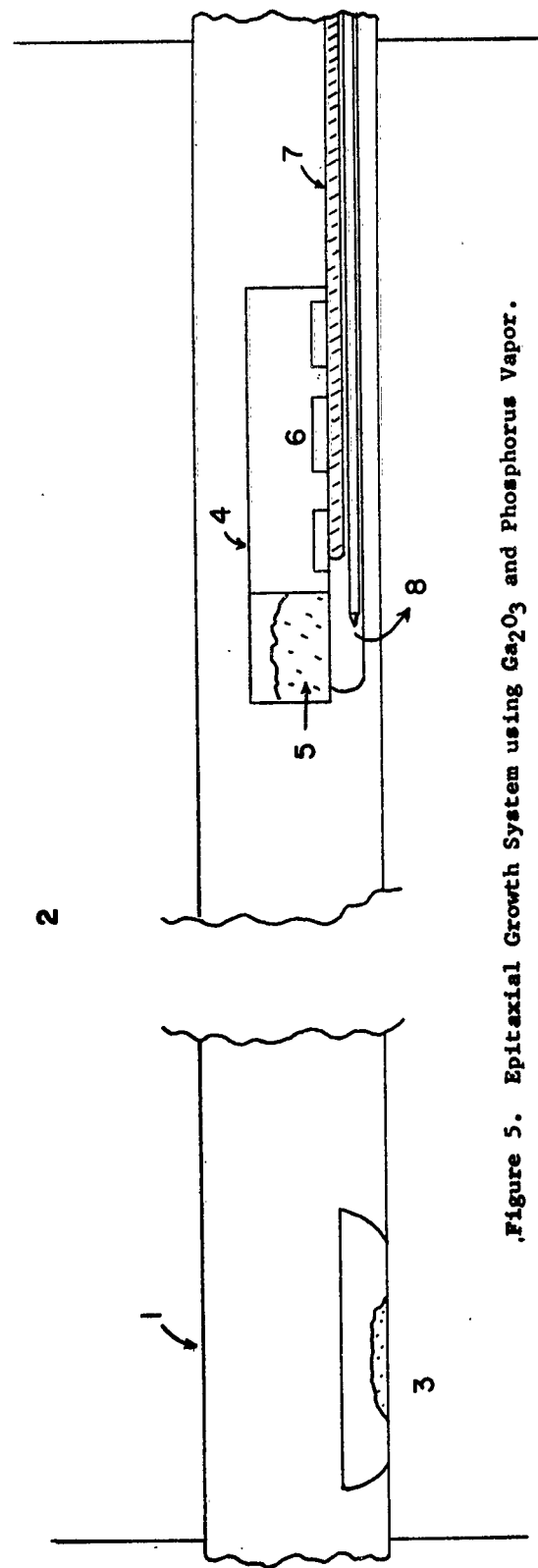


Figure 5. Epitaxial Growth System using Ga_2O_3 and Phosphorus Vapor.

1. Quartz Tube
2. 3-Zone Furnace
3. Phosphorus Charge
4. Quartz Boat Welded on Quartz Tube
5. Ga_2O_3 Charge
6. GaAs Wafers
7. Copper Heat Sink Inside Quartz Tube
8. Thermocouple Inside Quartz Tube



Figure 6. Laue X-Ray Pattern of 910°C Specimen.

The second method explored briefly was by iodine transport, in a sealed evacuated ampoule. The components of this system is illustrated in Figure 7. The substrates, source and elemental iodine, in a sealed ampoule was placed in a multiple zone furnace and a suitable temperature gradient imposed.

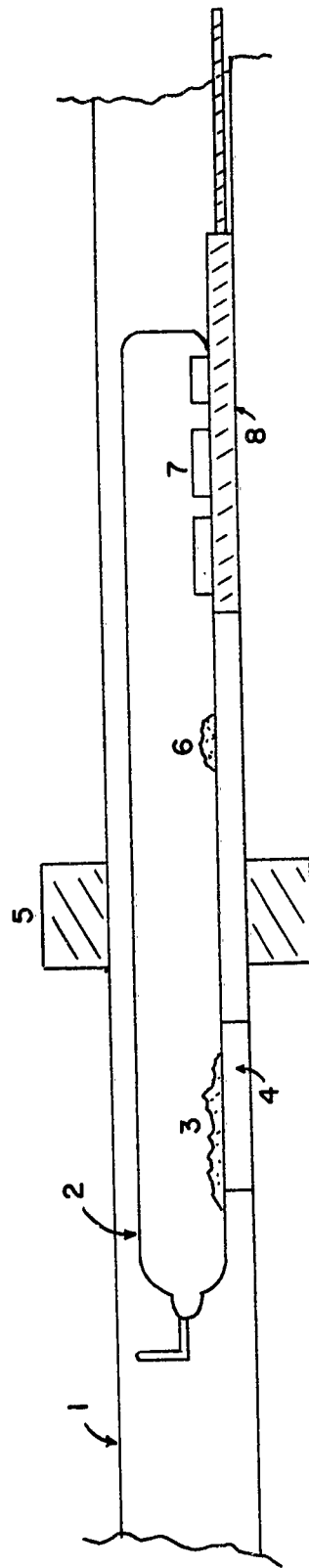


Figure 7. Iodine Transport Epitaxy System.

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.

Table V describes temperature schedules of two epitaxial runs using this method. System pressure was approximately 1 mm of iodine vapor.

TABLE V

Iodine Epitaxy Schedules.

<u>Item</u>	<u>Source Temp.</u>	<u>Substrate Temp.</u>	<u>Time</u>	<u>Epitaxial Growth</u>
Group 2,	840°C	700°C	120 Minutes	~ 60 Microns
Group 3,	700°C	630°C	15 Minutes	-

Results of the higher temperature run appear good. The low temperature run was carried out to determine the minimum of time and temperature. Growth was scattered, having the appearance of a deposit. Some small increase in temperatures must be contemplated, however, the technique appears attractive.

E. GaP Melt Growth Studies.

The need for high purity GaP for epitaxy, important for comparison of unijunction devices, is vital for the continuation of work on a 3-terminal device. Therefore some effort has been made during this work period to produce ingots of homogeneous, stoichiometric GaP ingots, of single crystal structure. The GaP, synthesized by passing phosphorus vapor over high purity Ga_2O_3 in a stream of hydrogen gas, is sintered at 1000°C for eight to ten hours to remove all volatile, non-reacted components in the material, and provide some aggregation in size. This charge is compacted, sealed in a fused silica ampoule, and placed in a high pressure furnace, illustrated in Figure 8. The charge is raised slightly above the melting point of GaP, held for one hour and cooled by slowly withdrawing from the hot zone, at a rate of approximately 0.013 inches per hour. The melted ingot is cooled slowly to approximately 600°C, then rapidly cooled to room temperature.

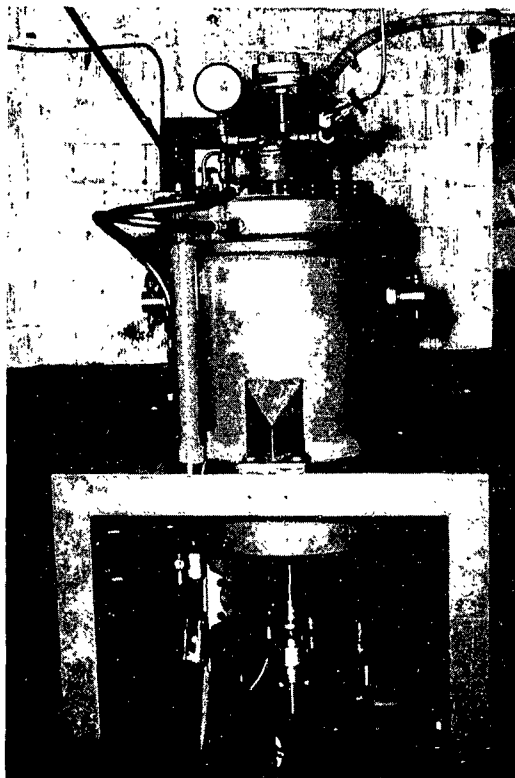


Figure 8. High Pressure, High Temperature Furnace.

Figure 9 illustrates such an ingot as grown. The ingot is etched briefly in dilute aqua regia and sliced. Typically, the ingot is clear except for the very top (The last end to solidify). Segregation effects usually produce a dark layer at the top, which includes any excess gallium or decomposition products. On occasion, where unreacted Ga_2O_3 remained in the charge, gallium inclusions have been observed in the top layer. Typically, the bottom sections are of multi-crystal structure, with crystallite growth expanding rapidly, so that the central portions are often of less

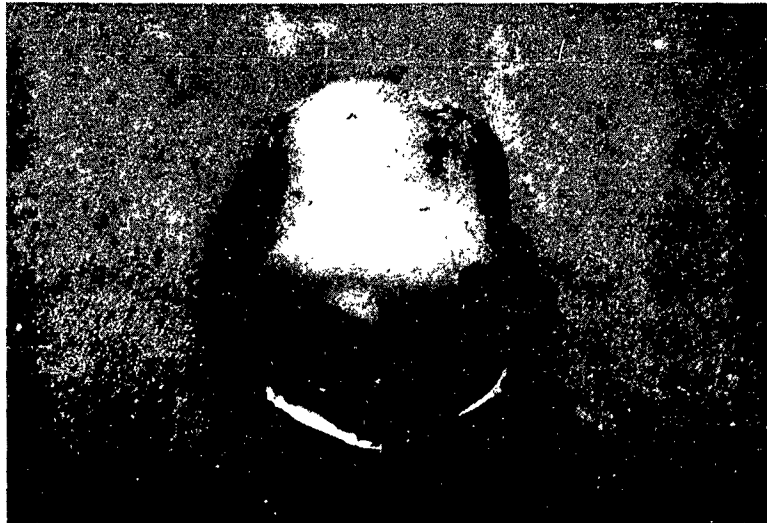


Figure 9. Melt Grown Ingot of GaP. (3x enlarged).

than four individual, twinned crystals. Crystal growth becomes granular or multi-crystal at the very top if significant inclusions are present. Crystal growth appears to be 1:1:1, preferentially. Figure 10 illustrates slices, unpolished to more clearly define crystal structure, of two ingots. Photography was by transmitted light. The bottom and top slices of the bottom series appear dark due to surface reflection; the material was essentially clear.

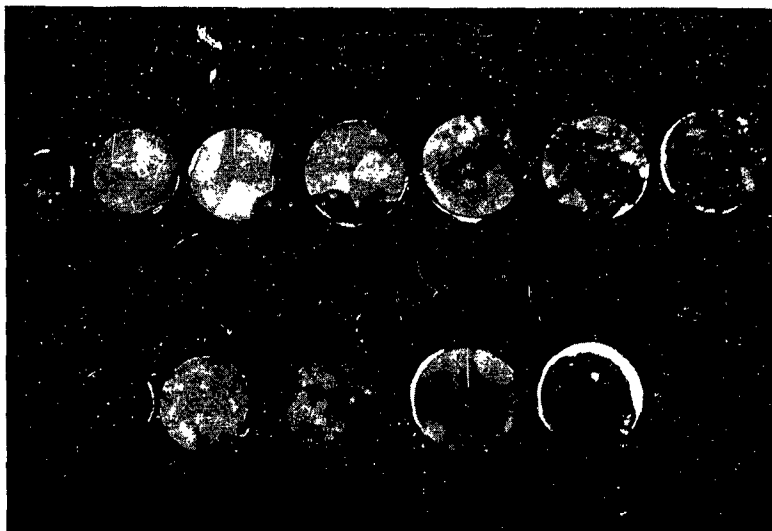


Figure 10. Slices of Two GaP Ingots by Transmitted Light.
(1 1/2x enlargement)

Spectro analysis indicates a wide range of total impurities, principally silicon. Total values of all impurities have ranged from a minimum of 1.6 PPM to 5000 PPM. Other than silicon, maximum total impurities have been less than 55 PPM. The high value of silicon is related to the amount, if any, of excess or decomposed gallium present, and its consequent attack of the silica container. When the charge has included unreacted Ga_2O_3 , silicon content is high, otherwise it is acceptably low.

F. Unijunction Devices.

Approximately 30 unijunction devices of variable gap and single gap structure were fabricated during this work period. The principal object of these was to evaluate the high temperature induction heating technique of zinc diffusion. For this reason, evaluation was chiefly concerned with sheet resistance of the diffused layer, diode characteristics and spectral response. Initial results were poor, due to poor regulation of zinc vapor. Sheet resistances were of the order of 1500 ohms per square. Use of a heavily zinc alloyed GaAs chip as a zinc source gave improved results. Sheet resistances of the order of 50 ohms per square were achieved, with corresponding improvement in diode characteristics. Spectral response and diode characteristics equal to the diffused type junctions were obtained in variable gap and single gap structures. Typical diffusion schedules were 750°C for four minutes.

Spectral response of variable gap devices #491 and #496 are illustrated in Figure 11. Of special interest is the very good response in the 0.5 to 0.6 region, with GaP layers of approximately 2-microns depth and the junctions 1-micron deeper. Figure 12 illustrates diode characteristics representative of these structures. Forward slopes are acceptably steep; some leakage currents are evident in the reverse curves. Edge etching appears to reduce this leakage and indicates it is probably due to damage from lapping the edges.

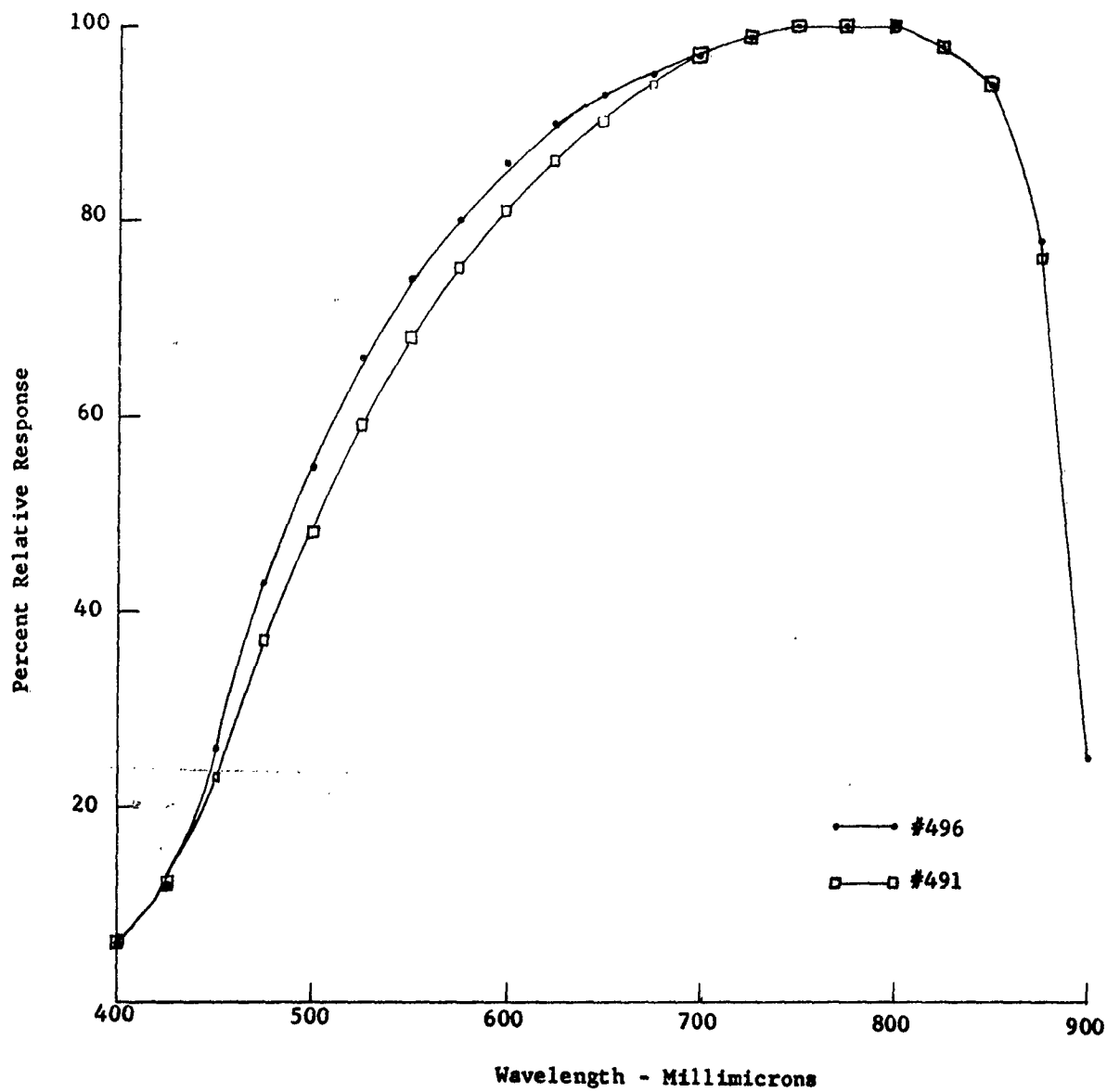


Figure 11. Spectral Response of Variable Gap Structures.

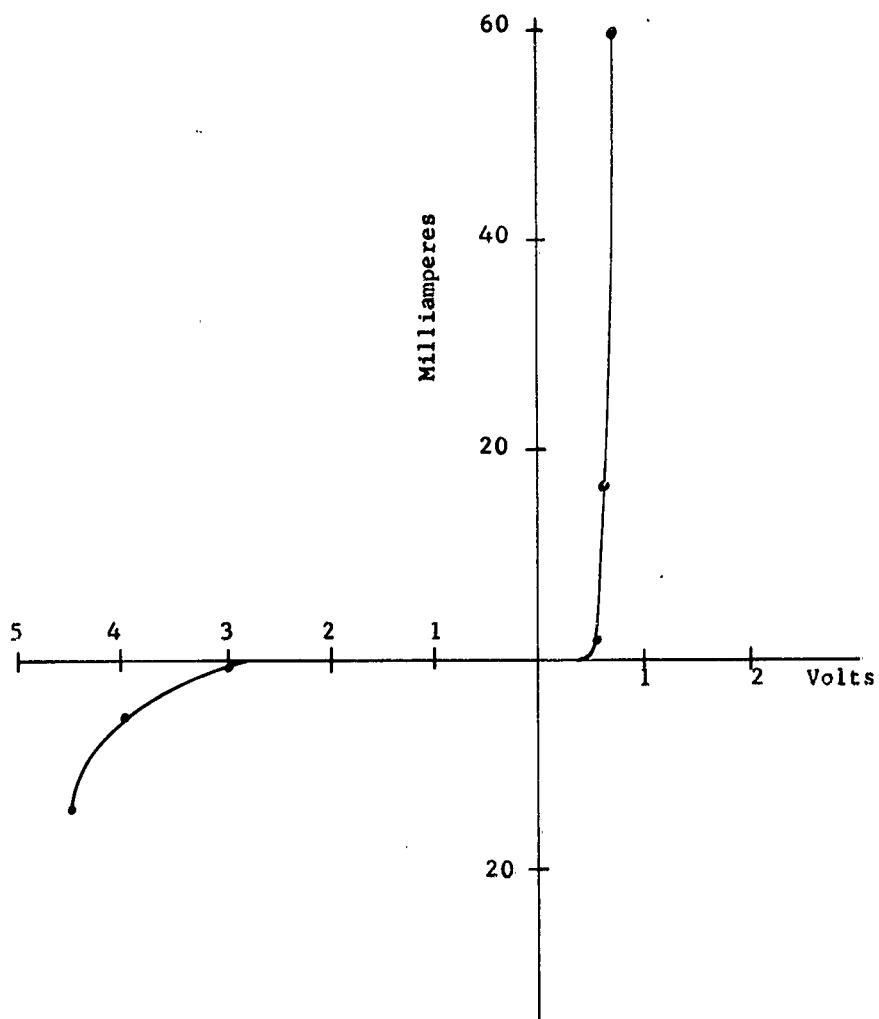


Figure 12. Diode Characteristics of Variable Gap Structure. #493.

G. Three-Terminal Devices.

Following the decision to investigate 3-terminal devices, effort was immediately directed toward fabrication of small area junctions, of the order of 1 x 2 mm size. Contact masking techniques for fabrication of mesa-type devices are presently being used to evaluate the junctions individually. Figure 13 illustrates a pattern of rectangular platinum contacts sputtered on two GaAs wafers. The rectangular geometry is for convenience only, circular masks are being prepared for subsequent use. These contacts are coated with zinc alloyed solder by dip soldering.

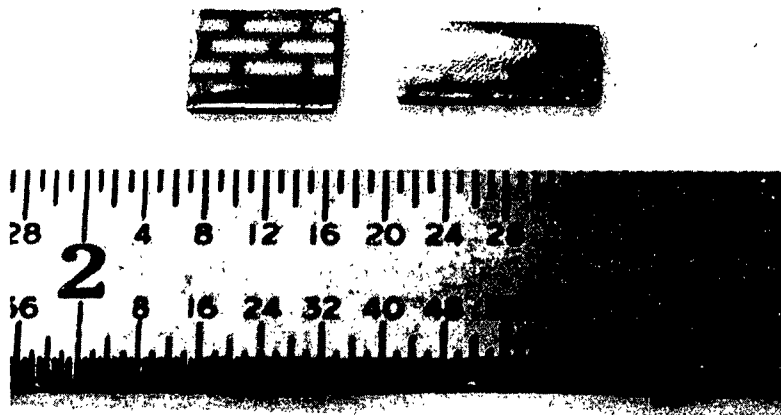


Figure 13. Sputtered Diode Pattern on GaAs Substrate.

Figure 14 illustrates a wafer with dip soldered pattern of contacts. The contacts are satisfactory in themselves as masks for the subsequent etching of mesas. Mesas are etched by a 70% H_2SO_4 , 15% H_2O_2 (30%), 15% H_2O solution. Individual dies are scribed from the pattern, and evaluated separately.

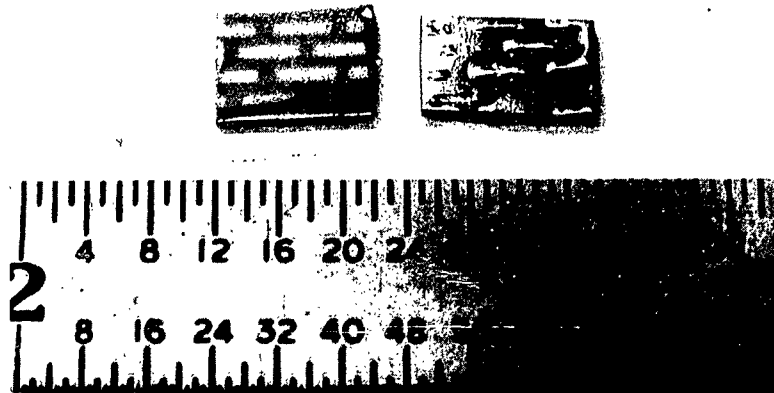


Figure 14. Dip Soldered Contact Masks Prior to Etching of Mesas.

Initial GaAs diodes were of n-type, 0.004 ohm-cm material. Zinc was diffused 900°C for 10 minutes to produce a junction of the order of 8-microns deep. Mesas, approximately 0.016 inches high were etched as described. Individual dies were sectioned, contacted and evaluated. Excellent diode characteristics were obtained, as illustrated in Figure 15.

Contacting and alloy junction studies are in progress, but incomplete at this time. More complete and precise report on this phase will be made at the end of the next work period.

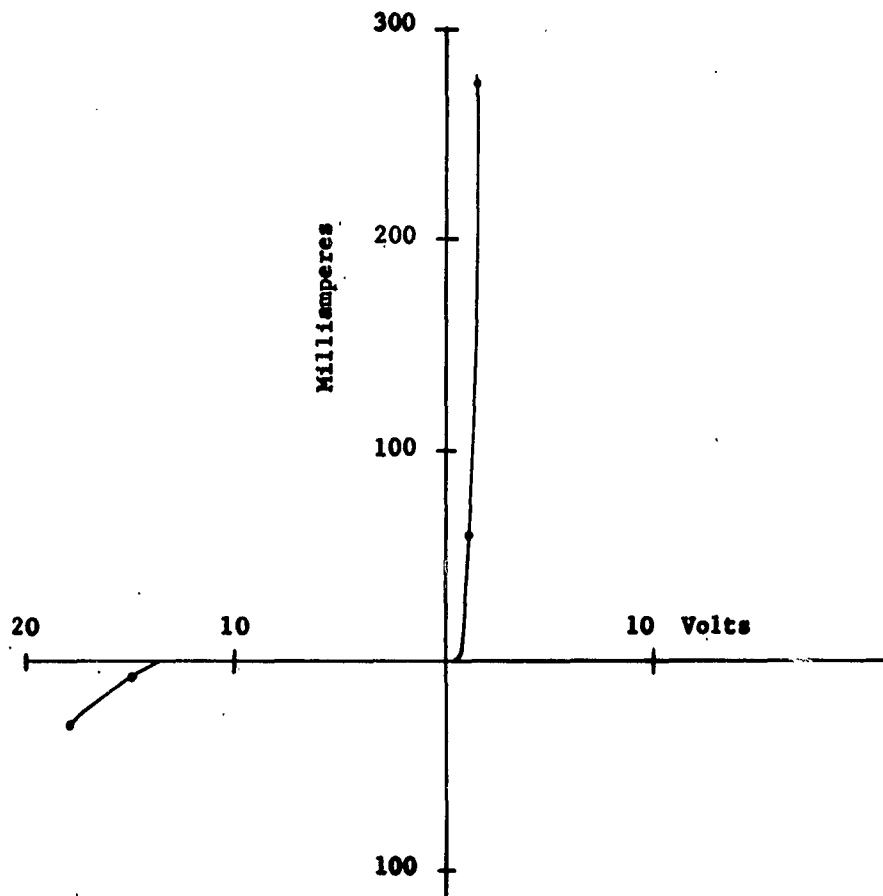


Figure 15. Diode Characteristics of Diffused Mesa Diodes.

H. Chemical Polishing and Etching.

The need for removal of damaged layers, and etching of mesa structures has resulted in the construction of a piece of apparatus for these purposes. The device is pictured in Figure 16. A Cenco Magnetic Stirrer is housed in a frame having a hinged top structure. The top structure has a 3-speed, reversing motor assembly mounted on it with a shaft terminating in a polyvinyl-chloride cylinder, arranged to place the cylinder near the side walls of a glass vessel containing the etchant and stirring rod. The subjects to be polished or etched are mounted with a low temperature adhesive, face down on the bottom surface of the polyvinyl-chloride cylinder, vertically oriented to clear the rotating stirring rod by approximately 1/8-inch. Specimens are routinely rotated oppositely in direction to the stirring rod for periods of the order of 30 minutes. Commonly, etchants such as $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ solution, or 10-20 percent bromine in methyl alcohol are used. Resulting surfaces are highly polished, (although not necessarily optically flat), undamaged and free of any oxide layers. The etchant, although not preferential, readily outlines any structural defects or anomalies. The same procedure is readily adaptable to mesa-etching. In this case, more concentrated solutions are used to expedite the dissolution of material.

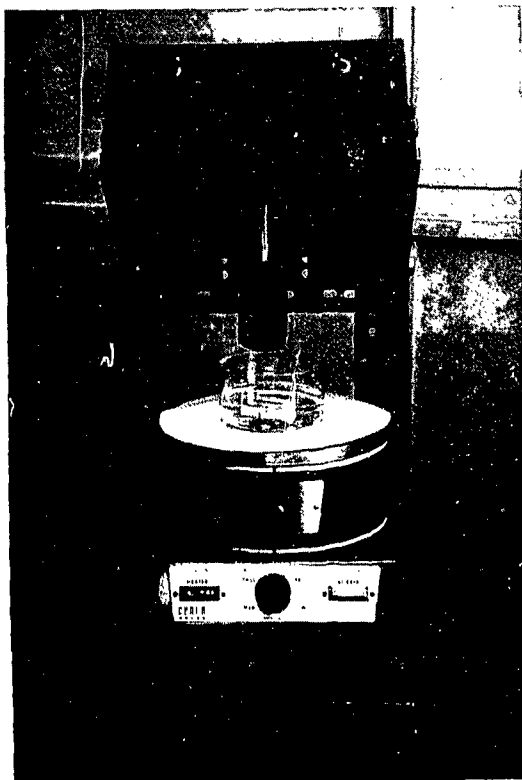


Figure 16. Chemical Polishing/Etching Apparatus.

V. SUMMARY

Considerable improvement in phosphorus purity has recently been made by careful selection of commercial material. The improved purity levels produced significantly less compensation in phosphorus diffused variable gap structures. The increased quality is expected to aid in the production of high purity GaP material for subsequent work.

The use of high frequency induction heating for diffusion and alloying offers significant advantages, although some further improvement in generation of vapor source techniques for the diffusion process could be made.

Epitaxial layers can be grown by simultaneous Ga_2O_3 synthesis-epitaxial growth techniques. Rather high temperatures are required; substrate temperatures affect growth rates, and reproducibility is judged poor. Epitaxy by iodine transport was carried out successfully; temperature requirements appear less stringent and are lower. Iodine or HCL transport are considered the more productive techniques.

The gallium phosphide melt growth technique has been improved and can produce acceptable material for epitaxy and/or direct device study. Significant improvement in ingot size and quality has been achieved.

Unijunction device structures were improved through use of higher purity phosphorus. Although effort is now directed toward 3-terminal devices, the use of the improved variable gap structure is feasible and available if desired. Initial exploration of 3-terminal structure is under way, and with the technology accrued thus far, may be expected to produce progress.

The mechanical apparatus and technique described herein for chemical polishing and etching is effective and efficient, and represents an improvement in uniformity and quality of device surfaces.

VI. FUTURE STUDIES

Future studies are planned to investigate the general efficiency of photon generation in two and three terminal devices, comprised of the gallium phosphide-gallium arsenide system. These studies are intended to determine the quantum efficiency, spectral distribution, etc., of such generation processes. Further data are to be obtained on the absorption and collection characteristics of a second sub-junction, with respect to doping levels, depths, etc.

Specific studies include the following:

- (a). Formation of "p" junctions in "n" type GaAs capable of generating photons under electric field excitation, and evaluation thereof. Both diffused and alloyed junctions are contemplated.
- (b). A study similar to the above, but involving opposite material types.
- (c). Formation of p-n and n-p junctions in gallium phosphide.
- (d). Epitaxial growth studies intended to produce single crystal layers of gallium phosphide, of selected type conduction, and GaAs substrates of suitable type conduction.
- (e). Junction formation in device structure produced as per Item "d" to culminate in an effective 3-terminal device.

Cognizance is taken that the above mentioned studies, carried out in detail, might be optimistic in so far as time is considered. It is considered that significant data on several of the studies have already accrued in the course of this investigation; some phases may be decided without extensive, exhaustive investigation and thus permit conclusive results.

VII. REFERENCE

- (1). Second Quarterly Technical Report - "VARIABLE ENERGY GAP
DEVICE", The Eagle-Picher Company. November 30, 1962.

VIII. PERSONNEL

Engineering Time Expended from November 1, 1962 to February
1, 1963:

Louis E. Stone,	432 Hours
George N. Webb,	420 Hours
William A. Ames,	67 Hours
J. S. Roderique,	120 Hours
Harold L. Allen,	1 Hour
Lloyd W. Brown,	24 Hours
John C. Budiselic,	11 Hours

Total Hours,	1,075 Hours
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3. Photovoltaic Devices
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