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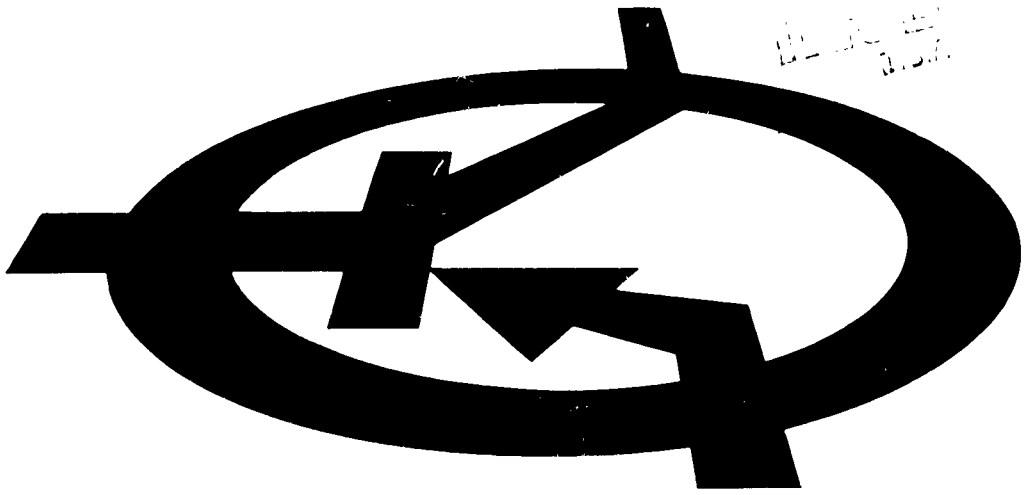

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June, 1963

INTERIM TECHNICAL DOCUMENTARY PROGRESS REPORT NO. 3
GALLIUM ARSENIDE EPITAXIAL FILM GROWTH

March 15, 1963 to June 15, 1963
CONTRACT NO. AF33(657)-9179

for

UNITED STATES AIR FORCE
MANUFACTURING TECHNOLOGY LABORATORY
AERONAUTICAL SYSTEMS DIVISION
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This Interim Engineering Progress Report covers the work performed under contract AF33(657) - 9179 from 15 March 1963 to 15 June 1963. It is published for information only and does not necessarily represent the recommendations, conclusions or approval of the Air Force.

The contract was initiated under ASD project 7-995 and is administered under the direction of E.H. Miller, ASRCTE of the Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Overall supervision of the program is being directed by Dr. R.B. Janes, Manager of the Advanced Development Laboratories. Mr. A.S. Rose, Manager of Materials and Processes, is the project manager. Mr. A. Mayer is the project engineering leader and Mr. W. Oshinsky the project engineer.

GALLIUM ARSENIDE EPITAXIAL FILM GROWTH

A third system intended for the preparation of high-resistivity GaAs was completed and put into operation. Six runs were made with iodine as the halogen transport agent for the gallium. No appreciable growth was obtained.

A small amount of Zn was added to the gallium of the trichloride system. Successive runs under identical conditions yielded steadily decreasing hole concentrations, ranging from high $10^{18}/cm^3$ carriers for the first run down to below $10^{16}/cm^3$ carriers for the seventh run. $ZnCl_2$, at temperatures ranging from 250°C down to 100°C, was used as the dopant. Variation in dopant vapor pressure yielded no commensurate change in hole concentration.

Hydrogen sulfide gas diluted with hydrogen was used as n-type dopant. Mixtures in the range 0.01-0.1% H_2S yielded layers which all contained electron concentrations of $4 \times 10^{18}/cm^2$.

A technique for making Hall effect and resistivity measurements on epitaxial GaAs layers was developed. The reflectivity method for measuring high carrier concentrations was refined and extended to the range of approximately 5×10^{17} to 10^{19} carriers/cm^3 for n-type material.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. PURPOSE

The purpose of this contract is to develop manufacturing processes and techniques to extend and bring under control the technology of epitaxial film growth for use in the producing of functional electronic circuits having small size, increased reliability, and lower cost.

II. TECHNICAL DISCUSSION

A. Surface Preparation

Surfaces prepared on the (100) plane are satisfactory and also, this plane is the best one for epitaxial growth. However, it is considered desirable to recheck growth on the (111) planes.

It is known that growth on the $(\bar{1}\bar{1}\bar{1})$ plane is slow and smooth but that deposition on the +(111) plane is rough and fast. During this report period an effort was made to prepare smooth surfaces on the +(111) face by an electro-mechanical polishing technique. Results are promising but additional work is required to produce wafers with surfaces satisfactory for epitaxial growth.

B. Apparatus and Vapor Sources

A third system, intended for the preparation of high-resistivity GaAs layers, was put into operation. Initially, the system incorporated three novel features: (1) a gallium bubbler for the removal of oxygen and water-vapor from the tank hydrogen carrier gas; (2) iodine as the halogen transport agent for the gallium; and (3) an AlN boat as the gallium container. The bubbler appeared to fulfill its principal function adequately. However, because large leaks were present in the system, oxidation of the gallium proceeded so rapidly that the bubbler was full of gallium oxide causing it to be blocked completely in a short time. Therefore, it was removed after the first day of operation and by-passed. A new bubbler is under construction. Hydrogen gas, purified by palladium diffusion, was then converted to the new system.

In all, the new system was run six times. Iodine temperatures were held constant at 80°C ± 2°C while gallium temperatures were varied from 550°C to 750°C. T-Zone temperatures were in the vicinity of

800°C, while the growth zone was between 700°C and 730°C. None of the runs resulted in any substantial amount of epitaxial growth. Since the rise of iodine in an open tube system did not appear promising, it was decided to convert the system to HCl and use it for p-type doping. The evaluation of the AlN boat used for the gallium is discussed in the section on evaluations.

C. Dopants

1. P-Type

Six mg of zinc were placed in a quartz boat containing 20 g of gallium metal. The boat was placed in the trichloride system, and eight successive one-hour runs were made under normal conditions. Four-point probe electrical measurements and thickness measurements by the angle lap technique were made. The first seven runs were p-type with steadily decreasing hole concentration, as shown in the plot of Figure 1. The eighth run was n-type. Theory predicts that zinc or hole concentration in the layer should fall off logarithmically with total running time of the system if the zinc is depleted more rapidly than the gallium. The linearity of the plot shows that this was true.

Although such a system of doping results in a wide range of carrier concentrations, it is impossible to control each run in such a way as to achieve a specific carrier concentration. The use of a slightly volatile Zn compound whose vapor pressure could be controlled within wide limits, offers the possibility of a more flexible method for making p-doped layers. $ZnCl_2$, whose vapor pressure was calculated and plotted over orders of magnitude, appears to offer this possibility (see Figure 2).

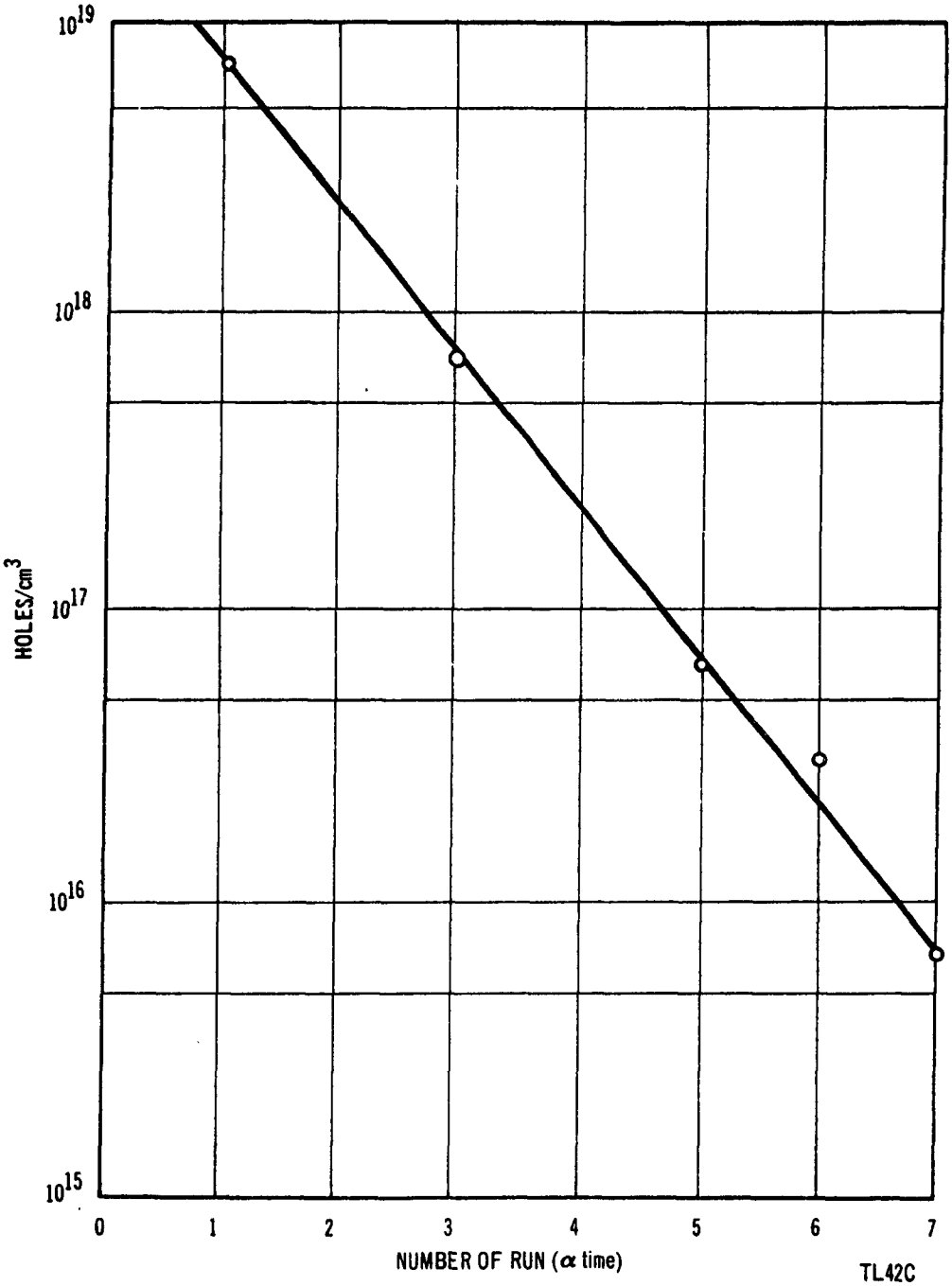

FIGURE 1 HOLE CONCENTRATION VERSUS RUNNING TIME – ZINC DOPED GALLIUM ARSENIDE

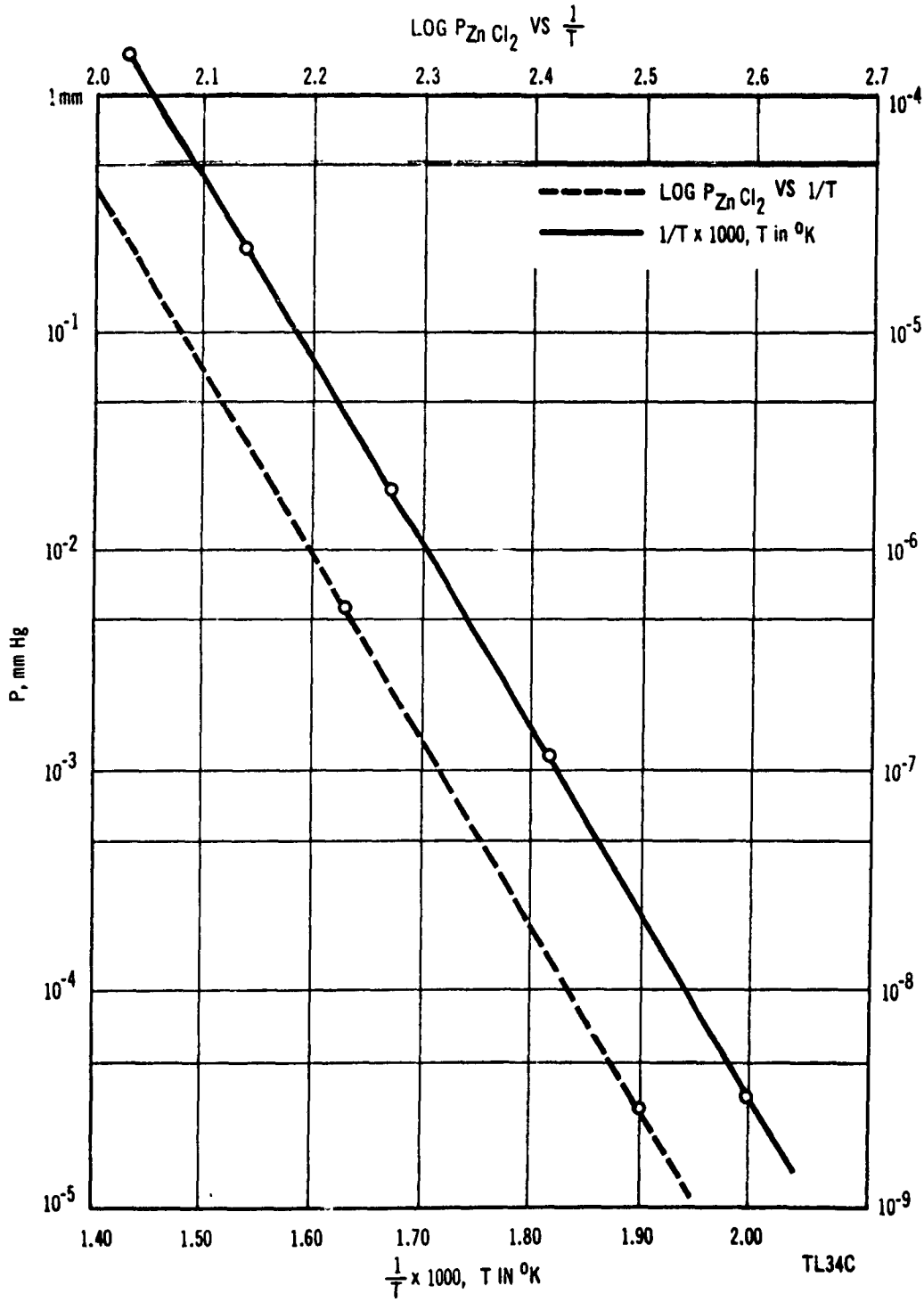

FIGURE 2 PLOT OF CALCULATED VAPOR PRESSURE OF $ZnCl_2$

– – – – 1 TO 10^{-5} mm AND 1.40 TO 2.00 $\frac{1}{T}$ x 1000 T SCALE

——— 10^{-4} TO 10^{-9} mm AND 2.00 TO 2.70 $\frac{1}{T}$ x 1000 T SCALE

Accordingly, a large quantity of $ZnCl_2$ was placed in the system in front of the gallium zone. A separate furnace controlled the $ZnCl_2$ temperature which was varied from 250°C down to 100°C. Angle lap and four-point probe measurements were made. Carrier concentrations are given for the first three runs with the $ZnCl_2$ at 250°C in Table I. The decrease in carrier concentration shows that the doping was not vapor-pressure controlled. For lower $ZnCl_2$ temperatures there was no significant variation in carrier concentration. After several runs, the appearance of the $ZnCl_2$ was altered, changing from a white to a gray powder. Presumably there was an interaction between $ZnCl_2$ and gallium chloride. In future runs with $ZnCl_2$, it will be placed on the arsenic side of the T.

TABLE I

CARRIER CONCENTRATION FOR $ZnCl_2$ DOPED LAYERS

No. of Run	$ZnCl_2$ Temp.(°C)	Carrier Concentration Holes/cm^3
1	250	1.0×10^{19}
2	250	6.9×10^{18}
3	250	3.8×10^{18}

2. N-Type

Hydrogen sulfide gas was used as a dopant in the system utilizing HCl. Dilute mixtures in the range 0.01 - 0.1% H_2S in hydrogen were used. Initially the mixtures were made up and stored in a glass tank equipped with suitable valves at a total pressure of 2.34 atmospheres. The tank was found to leak profusely which necessitated a fresh mixture of gases for each run.

Two stainless steel tanks were obtained and installed in parallel. Mixtures at a pressure of 3 atmospheres lasted from 6 to 10 runs, depending on the flow rate used. Another obvious advantage of the steel tanks is that it is safe to apply higher pressures which results in more gas being mixed and stored.

Fifteen runs were made with H_2S doping. Dilution and flow rates were varied from run to run in an attempt to change the sulfur concentration about one order of magnitude in the vicinity of carrier saturation. Since no prior data about the growth rates of such heavily doped layers or the efficiency of doping with H_2S were available, these initial H_2S doping runs were based largely on estimates.

Attempts to make electrical measurements on the early runs by the four-point probe method were unsuccessful because of point-contact rectification. Later, two other techniques of measurement, the Hall effect and reflectivity methods (described in detail below in the section on evaluations) showed that all the layers were in the carrier saturation range, $4 \times 10^{18}/cm^3$. In future runs more dilute H_2S mixtures will be used.

All the evidence accumulated during this period points to a carrier saturation level of $4 \times 10^{18}/cm^3$ for sulfur-doped gallium arsenide. For higher carrier concentrations, tin appears to be the most desirable dopant. Although no precise data are available, the solubility limit for tin in GaAs has been estimated to be in the 2 to $5 \times 10^{19}/cm^3$ range. By extrapolating vapor pressure data available in standard handbooks, it is

estimated that $SnCl_2$ near room temperature should enter the carrier gas in the proper concentration for making heavily doped layers.

D. Undoped Layers

For a period of several weeks before the $GaCl_3$ system was used for p-type doping, all undoped layers appeared to be highly contaminated. It was assumed that the $GaCl_3$ in the system at the time had been accidentally contaminated while being transferred from the zone-refining tube to the system. This was verified by the properties of the layers obtained when pure, fresh $GaCl_3$ was put into the system after cleaning it and re-converting it to undoped operations. Of the seventeen runs made to date since cleaning the system, very few layers with point contact breakdowns less than 50V have been obtained. The majority of the layers had breakdowns in the 50-70 V range, indicating electron concentrations in the vicinity of $10^{16}/cm^3$.

E. Evaluation

1. Surface Finish and Thickness

During the first half of the period covered by this report the incidence of air leaks in the lines and systems was exceptionally high. At that time, the systems and lines were being opened frequently to permit additions or modifications. As a consequence, the expected deterioration in both surface finish and growth rate occurred. In many cases, optical interference patterns could not be obtained by the I.R. reflection method. It was then necessary to use angle-lap and staining techniques for the measurement of thickness.

During the latter half of this period less contamination by air and water vapor was evidenced. Most of the layers, both doped and undoped, had excellent finish and growth rates were generally normal, i.e., 8-14 μ/Hr. Prior experience has shown that heavy doping with a halide reduces the growth rate. Thus, for some impurities present in a concentration above mid- $10^{18}/cm^3$, a loss in growth rate of 50% or more is expected.

2. Electrical Measurements

With the exception of high resistivity material, resistivity measurements by the four-point probe method are feasible for p-type gallium arsenide. Rectification effects between the metal probe and n-type GaAs preclude the possibility of accurate electrical measurements using a four-point probe. Thus, for an n-type layer on a non-shorting (i.e., high ρ or p-type) substrate, it is necessary to apply non-rectifying soldered leads to the surface of the epitaxial layer in order to make electrical measurements. Such a technique was used on a bridge specimen Cavitroned from an H_2S-doped epitaxial layer deposited on a p-type substrate. The entire wafer was then covered with lacquer, which was removed only from those spots on the layer surface where the contacts were to be applied. Nickel was deposited on these open spots by electroplating. Wires were then indium-soldered to the nickel dots. Resistivity and Hall measurements were made on the epitaxial brige. A thickness measurement was also made by angle-lapping and staining a portion of the wafer retained for that purpose. An electron concentration of $4 \times 10^{18}/cm^3$ was obtained, indicating carrier saturation.

The electron mobility was 700 cm^2/volt-sec, indicating a total ionized impurity content of about $7 \times 10^{19}/cm^3$. In order to reduce the electron concentration to below the saturation level[1], the H_2S concentration of the doping gas which was .0175 volume % in this case, must be reduced by a factor of at least 20. In the next series of runs, H_2S concentration in the range of 0.0001 - 0.001% will be used.

3. Optical Measurements

The epitaxial layer from which the Hall bridge specimen was taken was one of two wafers coated in the same run. As a check, the second wafer was measured by the optical reflectance method. The electron concentration obtained optically was $4 \times 10^{18}/cm^3$.

A new instrument, the Beckman IR5A Spectrophotometer with a cesium bromide prism was used for the reflectance measurements. The range of the instrument is from 11μ to 35μ. A new set of reflectance curves was run for n-type specimens of known electron concentration. Instead of the wavelength for 50% reflection (λ 50%) used as a calibration value in the last Quarterly Report, the wavelength for minimum reflectance (λmin) was used.[2] The use of λ min has two advantages: (1) λ min is always less than λ 50%, making it possible to measure somewhat lower carrier concentrations ($\sim 5 \times 10^{17}$ electrons/cm^3) before reaching 35μ, the highest wavelength obtainable on the apparatus; and (2) data from the literature can be included in the calibration curve, since λ min has been used by other researchers[3]. Figure 3 is

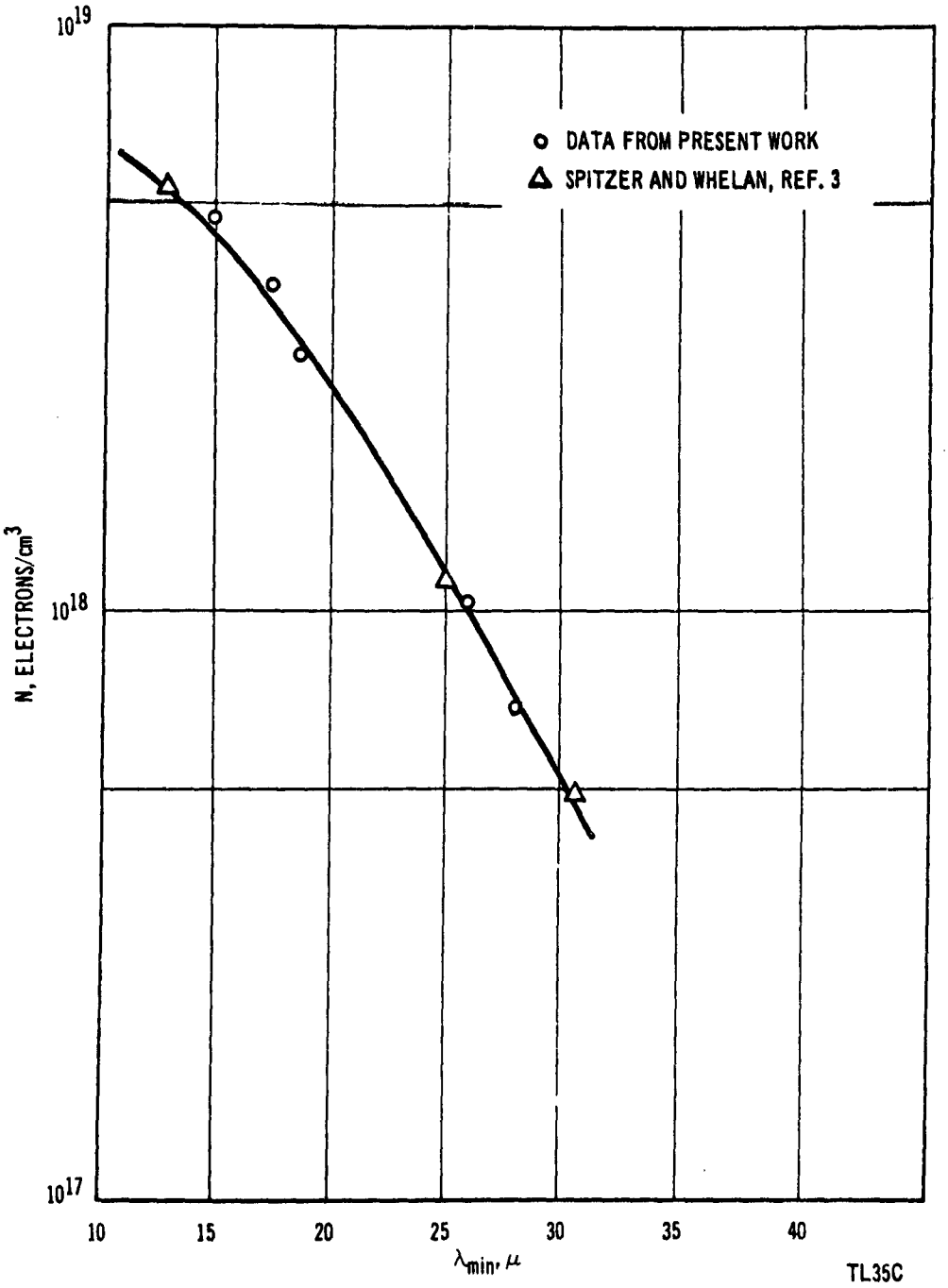

FIGURE 3 ELECTRON CONCENTRATION VERSUS WAVELENGTH OF MINIMUM REFLECTION

a plot of electron concentration vs. λ min.

Four n-type layers which were heavily doped with sulfur using H_2S in concentrations ranging from 0.01% to 0.1% were checked by the reflectance technique. All had electron concentrations of $4 \times 10^{18}/cm^3$, which appears to be the maximum carrier concentration obtainable with this dopant.

The new apparatus for measuring electron concentration in the 10^{15} to $10^{17}/cm^3$ range by the saturated surface photovoltage method has been put into operation. Initial attempts to obtain data have been unsuccessful because of the presence of large stray voltages. It is not clear whether the highly sensitive DC meter is at fault or there is an unpredictable contact potential. The stray voltage encountered was variable and often considerably higher than the surface effect to be measured. If further attempts do not yield results, the single apparatus used previously will be utilized.

4. Spectrochemical Analysis

An evaluation of the purity of the Ga and GaAs in the new system was made by means of emission spectroscopy. Table II shows the impurities determined and the estimated concentrations of those detected.

The faint trace of magnesium found in the gallium is always present in the purest samples and is presumed to be the minimum background value.

TABLE II

ESTIMATED IMPURITY CONCENTRATIONS IN ppm BY WEIGHT, SAMPLE EI-6

Element	Sample	
	Ga	GaAs
Si	N.D.[a]	10
Pb	N.D.	15
Mg	F.T.[b]	1-2
Ni	N.D.	N.D.
Fe	N.D.	N.D.
Al	N.D.	N.D.
Cu	N.D.	N.D.
Zn	N.D.	N.D.
Sn	N.D.	N.D.

a. Not detected

b. Faint trace

III. PROGRESS OF WORK

The following chart indicates the objective and degree of completion for the areas as listed.

Objective	% Complete	Remarks
Surface Preparation		
1) Removal of work damage	100	-
2) Removal of surface impurities	100	Continued feed back from RCA supported surface studies.
Vapor Source	100	Possible use of I_2.
Doping		
1) n-type 10^{16} - 8 x 10^{18} ± 15%	75	Maximum now 3.7 x 10^{18}, minimum 8 x 10^{16} limited by contamination. Control no better than ± 50% at present.
2) n-type 10^{14} - 10^{16} ± 15%	75	Excellent control when contamination not present using arsenic pressure control.
3) p-type 10^{14} - 5 x 10^{19} ± 15%	60	Work being initiated.
Dislocation 1,000 cm^{-2} max.	-	No etch for dislocation on (100) plane, found or reported.
Surface Imperfections		
Planarity to 0.1 μ over 2 cm^2	85%	Most wafers free of imperfections at present. No measurements on wafers 2 cm^2 in area.
Lifetime		
.001 to 0.01 μ-sec. related to N_{DA} and heat treatment	-	Measurement techniques available, work not started.
20 wafers/run 2 cm^2	25%	Very few wafers 2 cm^2 in area; work delayed by difficulty with surface imperfection. Have made 5 wafers per run

IV. CONCLUSIONS

1. Iodine does not appear to be useful as the halide transport agent for gallium in an open tube system.

2. Neither Zn metal nor $ZnCl_2$ appear to give the desired control over doping level when inserted into the gallium side of the T.

3. H_2S is a suitable doping material. The saturation level for electron concentration is $4 \times 10^{18}/cm^3$ when sulfur is the n-type dopant.

V. PROGRAM FOR NEXT INTERVAL

1. Evaluate gallium bubbler for hydrogen purification.

2. Try doping with $ZnCl_2$ on the arsenic side of the T.

3. Continue H_2S doping at lower concentrations.

4. Determine possibility of using (III) oriented substrates.

5. Determine capacity limits of present system.

VI. BIOGRAPHY

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A. S. Rose received both the B.S. degree in 1935 and M.Ch. E. in 1939 from New York University.

Mr. Rose was employed with the National Bureau of Standards and the Williams Gold Refining Company. He joined RCA in 1942 as a metallurgist and left in 1950 to go with ITE Circuit Breaker Company. He resumed his service with RCA in 1955 holding the same position. Mr. Rose was promoted to his present position in July 1956.

Mr. Rose has written many articles on metals which were published in technical journals and magazines.

VII. REFERENCES

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