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HIGH-TEMPERATURE-MATERIALS STUDY

By R. D. Baxter, E. P. Stambaugh, and F. J. Reid

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INTRODUCTION

This is the Final Technical Report on the subject program and covers the research accomplishments from March 1, 1966, to December 31, 1967. The primary objective of this investigation is to provide knowledge useful for producing solid-state electronic devices that can be operated at higher temperature than is possible with currently available semiconducting materials and devices.

A material for electronic devices capable of operation at high temperatures must possess a wide forbidden gap such that the concentration of intrinsic carriers at the operating temperature is small compared with the density of extrinsic carriers. The material must also exhibit a low vapor pressure and a low dissociation pressure at the operating temperature. Finally, the material must be amenable to preparation in single-crystal form of sufficient purity to permit fabrication of useful device structures.

The material under investigation is the III-V compound semiconductor AlP, which has a forbidden band gap of approximately 2.5 ev and a melting temperature in excess of 2000 C.

Principal emphasis during this program was on the development of chemical vapor-deposition techniques for the growth of single-crystal AlP of sufficient purity to permit a meaningful evaluation of the usefulness of AlP in high-temperature-device applications.

EXPERIMENTAL DETAILS

High-Temperature Reactor

In view of the high melting point (>2,000 C) and high dissociation pressure of AlP at the melting point, a reasonable approach to the problem of synthesizing monocrystalline AlP of high purity is that of chemical vapor deposition (CVD). With CVD techniques, the problem is no longer one of forming AlP, but rather is one of transporting the compound, or its intermediates, to a desired deposition site.

Previous work at Battelle-Columbus[1]* indicated that AlP could be successfully deposited onto suitable substrate materials (e.g., silicon) by a vapor-phase process which involved:

(1) Reacting molten Al with a halogen to form volatile aluminum halides

(2) Transporting the halides through an open-tube flow system using hydrogen as a carrier gas

(3) Reacting the aluminum halides with phosphorus vapor in a vapor-growth chamber containing the substrate to form an epitaxial layer of AlP.

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*References are given on page 31.

HIGH-TEMPERATURE-MATERIALS STUDY

By R. D. Baxter, E. P. Stambaugh, and F. J. Reid

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Columbus, Ohio

SUMMARY

Techniques were developed for the chemical vapor deposition of aluminum phosphide (AlP) onto single crystals of Si and GaAs at substrate temperatures in the range 650-1200 C. For deposition at substrate temperatures above 950 C, AlI and PH_3 were reacted in an essentially all-ceramic reactor system, designed and built in the course of this program. In this system, substrate temperatures, temperature gradient at the substrate, and phosphorus-to-aluminum ratio (vapor concentration) appeared to be controlling factors in achieving single-crystal deposits. Epitaxial layers up to 600 microns thick were grown on silicon substrates at 1120 C in a temperature gradient of about 10 deg/cm for a phosphorus-to-aluminum ratio less than unity. The resulting material generally exhibited free-electron concentration on the order of 1×10^{18} cm^{-3} and electron mobility as large as 80 cm^2/v-sec. This represents a substantial improvement over the properties observed in material grown by the same process in an all-quartz reactor. Spectrographic analyses indicated that the improved electrical properties were associated with reduced concentrations of chemical impurities, particularly silicon and copper, and identified silicon as the major donor impurity. The lowest silicon concentration achieved with the ceramic reactor was about 30 ppm or 1.5×10^{18} cm^{-3}.

Specimens of AlP prepared in the ceramic reactor were used for exploratory studies on p-n junction formation and device fabrication. Work with point-contact diodes provided encouraging information about the electrical and chemical stability of AlP upon thermal cycling to temperatures up to 1000 C.

The feasibility of producing AlP of still lower silicon content by (1) deposition at substrate temperatures below 950 C and (2) use of induction heating of the substrates (to maintain the reactor walls at a relatively low temperature) was investigated employing the reagent systems PH_3-$AlCl_3$ and Al-PCl_3. Crystalline AlP was deposited as layers onto GaAs, silicon, and tantalum by the PH_3-$AlCl_3$ reaction at substrate temperatures as low as 650 C. Electrical measurements on such layers revealed carrier concentrations as low as 3.5×10^{16} cm^{-3} with corresponding mobility of 98 cm^2/v-sec.

Layer growth was not achieved with the Al-PCl_3 system. However, needles grown at 925 C by this reaction, using a Lucalox boat and reactor liner, contained only 10 ppm silicon: the lowest level of silicon contamination achieved under this contract.

It is concluded, on the basis of the results of the rather modest effort expended thus far, that AlP shows excellent potential for development as a material for devices with superior high-temperature characteristics. Active pursuit of its further development is recommended.

The important features of such a flow system using iodine as the halogen and PH_3 as the phosphorus source are shown in Figure 1.

The initial system employed a quartz reaction chamber, and at the relatively high temperatures encountered in zones T_2 and T_3 of Figure 1, the quartz walls were etched by the corrosive vapors, which resulted in high concentrations of unwanted impurities, particularly silicon, in the deposits. AlP prepared in the quartz reactor generally contained 1000 ppm (5×10^{19} cm^{-3}) silicon donors[2].

In the course of the program reported here, two approaches to the problem of producing layers of increased purity were followed. The first approach involved the elimination of quartz parts from the high-temperature zones of the reactor.

Figure 2 is a schematic of a system, designed and built for this program, which contains only Al_2O_3 ceramic parts in the high-temperature zones. The predominant vapor flow is from left to right in the reactor. The system employed hydrogen as a carrier gas for the iodine at typical flow rates of 500-1000 cm^3/min. Typical flow rates for the PH_3 + H_2 mixture were in the range 20-100 cm^3/min. The inlet tube directs the PH_3-H_2 mixture through a region of the furnace in which the PH_3 dissociates into P_2 and H_2 and conducts these vapors into the reaction chamber at a point between the aluminum source and the substrate. Some back diffusion of phosphorus occurred at this point, to a degree determined by the difference between the flow rates of the H_2 + I_2 gas and the PH_3 + H_2 mixture. Unless this difference exceeded about 450 cm^3/min, the phosphorus diffused far enough upstream to reach the aluminum source. When this occurred, a layer of AlP formed over the surface of the aluminum, which impeded the reaction of aluminum with the iodine.

Figure 3 shows in detail the design of the stainless steel end caps that were fitted on each end of the ceramic reactor with vacuum-tight O-ring seals. The end caps provided entrance ports (ceramic tubes fitted with O-rings) and a stainless steel exhaust port (not shown). Under operating conditions, the temperature of the end caps was 50-100 C.

A difficulty encountered with the reactor shown in Figure 2 was that the large-diameter tube would usually break after one or two deposition runs. The break occurred at a position, about 20 cm downstream from the left end of the furnace, where a steep temperature gradient existed and AlP formed on the tube wall. Thus, it was necessary either to replace the tube (which generally involved modifying the end caps to fit the new tube) or to use an alumina liner inside the reactor and replace the liner after one or two experiments.

Except for the breakage problem just described, however, no serious problems were encountered, and the results obtained with the ceramic reactor were encouraging. The level of silicon contamination was decreased from the previous level of 1000 ppm to about 30 ppm (1.5×18 cm^{-3}) in AlP layers grown epitaxially on Si, GaAs, and GaP substrates. The system was also used to gather potentially useful fundamental information on the effects of substrate temperature, temperature gradient at the substrate, phosphorus-to-aluminum ratio, etc. on the growth process.
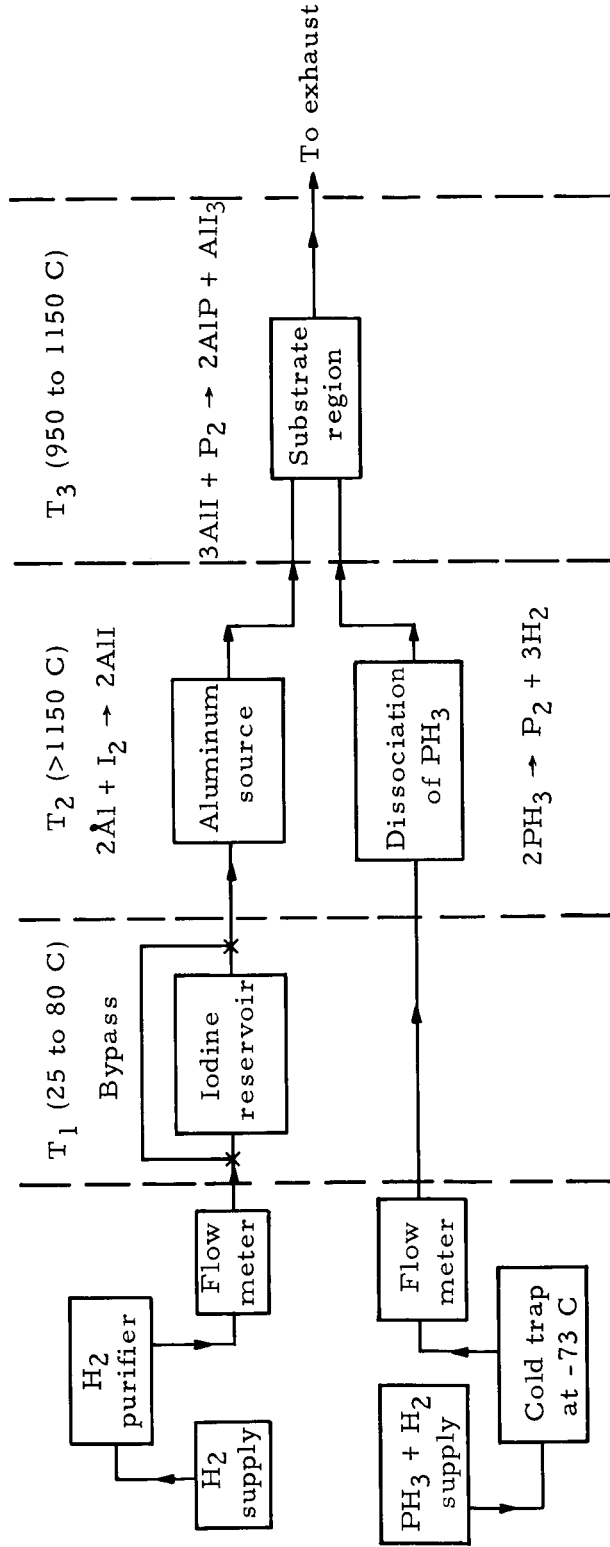
FIGURE 1. SCHEMATIC REPRESENTATION OF VAPOR FLOW SYSTEM FOR DEPOSITION OF AlP

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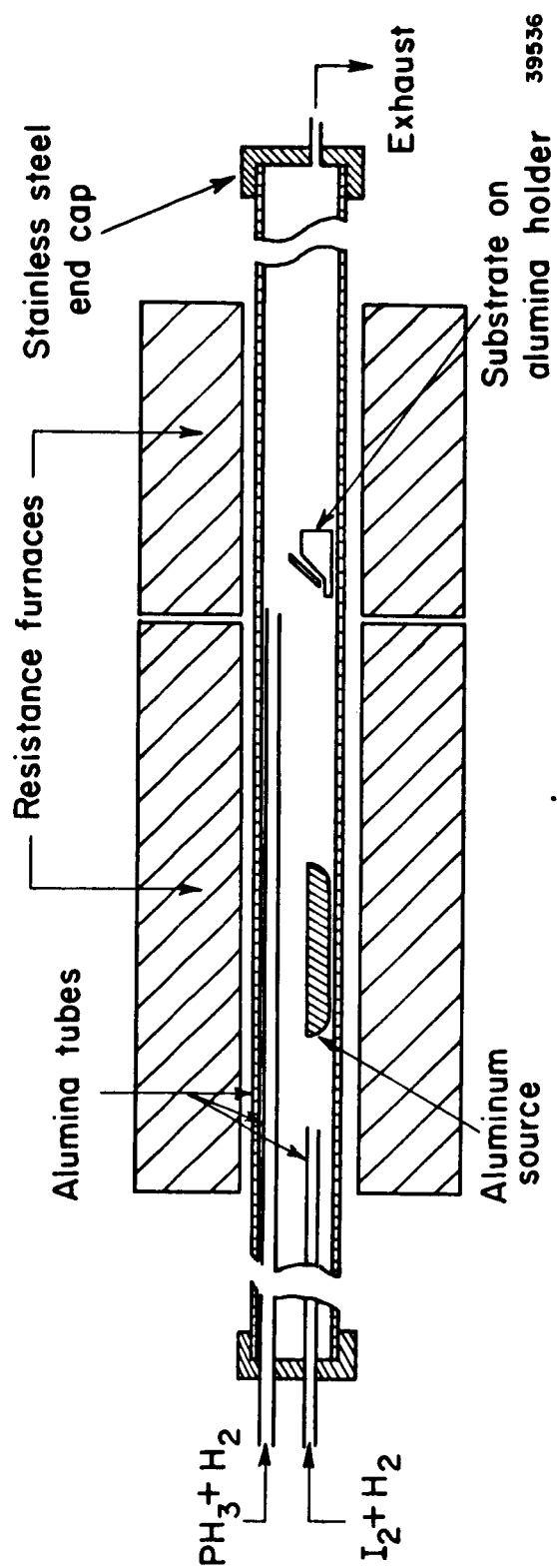
FIGURE 2.   SCHEMATIC OF REACTOR SYSTEM

Scale ≈1:3.
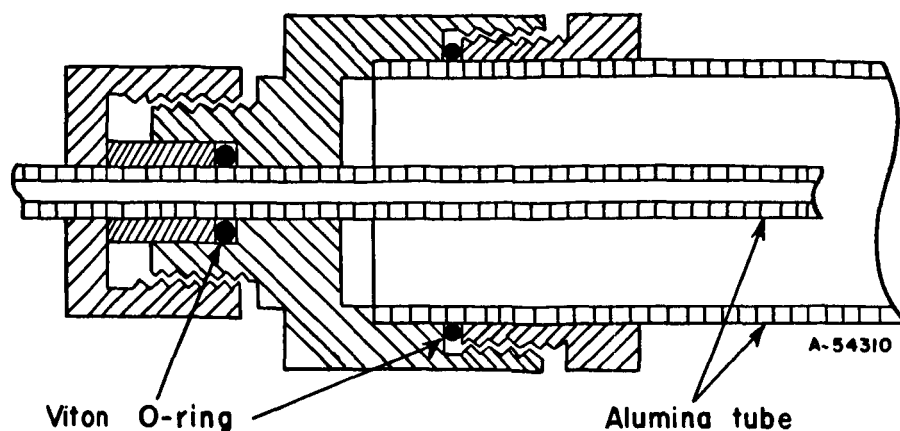
FIGURE 3. SCHEMATIC OF STAINLESS STEEL END CAP

Full scale.

Low-Temperature Reactor

Toward the latter stages of the program, it became clear that a further reduction in impurity content might best be attained by

(a) Rebuilding the AlI-PH₃ reactor using higher purity ceramics
     (e.g., Lucalox)

(b) Developing a lower temperature deposition scheme to avoid the
     high-temperature interaction between corrosive vapors and
     reactor walls.

Since a "low"-temperature reactor can also be built of high-purity ceramic, Method (b) clearly has more potential for producing a high-purity product. The past few months of the program were accordingly devoted to development of such a system.

The systems $Al-PCl_3$ and PH_3-AlCl_3 were considered in the development of a low-temperature method for the vapor deposition of AlP of improved purity. Essentially three steps were involved in the low-temperature depositions. The first step was the formation of a volatile complex. The second step was transporting the complex to a deposition site, and the third step was the decomposition of the complex to form crystalline AlP.

A diagram of the equipment used to deposit AlP by the $Al-PCl_3$ reaction is presented in Figure 4. Since the primary goal of this phase of the investigation was the formation of AlP of improved purity rather than crystalline perfection, epitaxial growth onto substrates was not attempted. Instead, the AlP was vapor deposited in the vicinity of the aluminum melt, which was heated to the reaction temperature by direct coupling to the aluminum using a 10 KVA induction heater. By using induction heating, the reactor walls could be maintained at a low temperature relative to that of the aluminum

melt, thus reducing the probability of contamination. The reaction tube was constructed of fused silica. To reduce still further possible contamination of the product, the aluminum melt was contained in a Lucalox* boat, which was isolated from the fused-silica reaction tube with a Lucalox liner. Hydrogen (flow rate controlled by a rotameter) was purified by passing it through palladium, and last traces of water were removed by passing the purified hydrogen through a liquid-air trap. Loading and unloading of the reaction tube were facilitated by a glass joint at the end of the reactor tube.

A schematic of the apparatus used for the vapor deposition of AlP by the $AlCl_3$-PH_3 reaction onto an inductively heated substrate is shown in Figure 5. The furnace was a multizone, nichrome-wound resistance furnace. Each zone was controlled independently. The reaction tube was constructed of quartz. The $AlCl_3$ was contained in a fused-silica, open-end, covered boat. Hydrogen was purified by first passing it through palladium and then through a liquid-air trap to remove the last traces of water. PH_3 was dried by passing it through a CO_2-trichloroethylene trap. A ground-glass joint at the end of the reaction tube facilitated loading and unloading. The susceptor holder was constructed of lavite or Al_2O_3. Susceptor materials were graphite, silicon, or tantalum, whereas substrates were either silicon, tantalum, graphite, or GaAs.

Substrate Preparation

The silicon substrates were generally high-resistivity, (111) or (100) oriented single crystals about 3/4 inch in diameter. High-resistivity silicon was used predominantly because it can be polished to a finer finish than can heavily doped silicon. After lapping the saw-cut surface with SiC paper, the silicon was given a final chemical polish by rotating it at 100 rpm in 9:1 HNO_3:HF. After polishing, the substrates were boiled in trichloroethylene for 2 minutes. The hot bath was then ultrasonically agitated for 2 minutes. The substrates were then immersed in ultrasonically agitated methyl alcohol and given a final rinse in filtered deionized water.

GaAs substrates were similarly prepared except that the chemical polish consisted of 1:1 HCl : HNO_3.

The substrates were stored immersed in n-butyl alcohol until ready for use.

Purity and Handling of Starting Materials

The aluminum used is obtained commercially** as 99.999 percent pure. It is cut into pieces to fit into high-purity Al_2O_3 boats which have a capacity of about 5 cm^3. Prior to loading, the aluminum is lapped on 600-mesh SiC paper and etched in boiling 9:1 H_3PO_4:HNO_3 for about 10 minutes. After loading, the aluminum is heat treated at 1100 C under a fore-pump vacuum for 30 minutes. Approximately 0.05 to 0.1 gram of the total charge of 10 grams of aluminum is evaporated in the course of this heat treatment.

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*Lucalox is the trade name for a polycrystalline alumina material. Purity of Lucalox is 99.9 percent Al_2O_3.
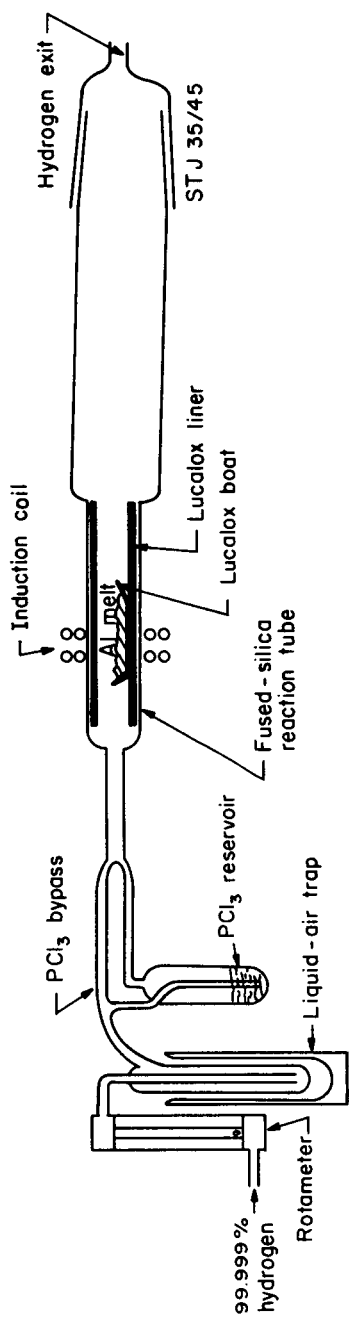**AIAG Metals, Inc., New York, New York.

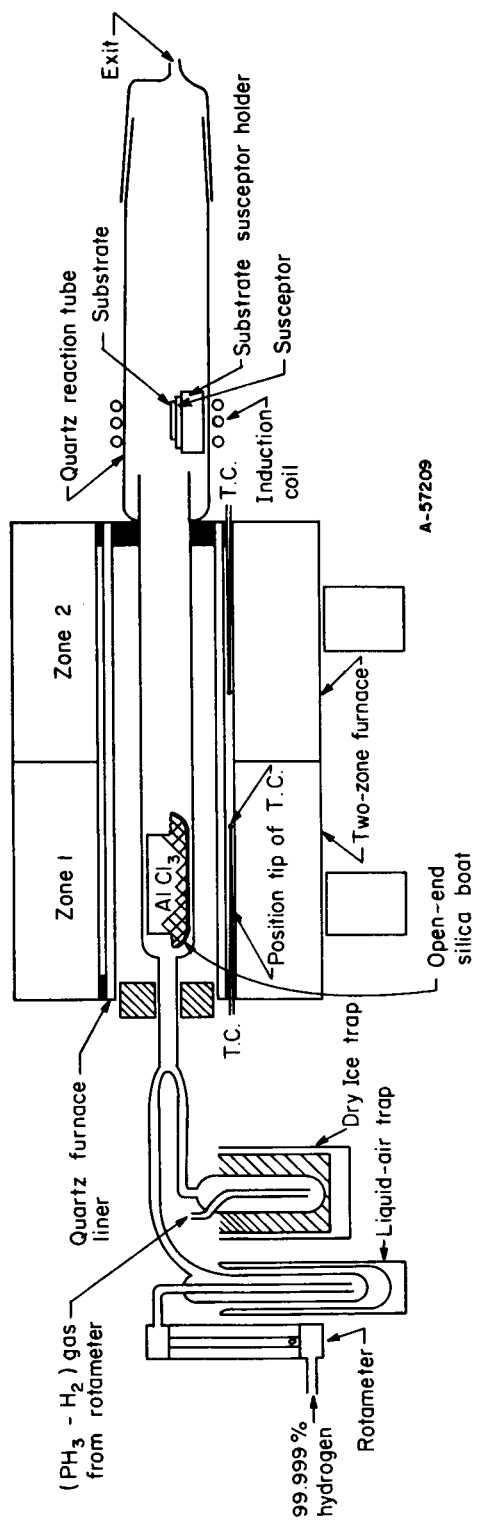FIGURE 4. Al-PCl$_3$ LOW-TEMPERATURE REACTOR

A-57209

FIGURE 5. AlCl$_3$-PH$_3$ LOW-TEMPERATURE REACTOR

The iodine used to transport the aluminum in the high-temperature reactor is obtained commercially* as 99.9999 percent pure, and enough iodine (300 grams) for several experiments is placed in a U-shaped Pyrex reservoir. Figure 6 shows schematically the iodine reservoir and iodine transport rate as a function of temperature when hydrogen is passed through the reservoir at 500 and 1000 cm^3/min. The source of the hydrogen carrier gas is commercially available tank hydrogen which is purified by diffusion through palladium. The hydrogen flow is controlled and monitored by a flowmeter located upstream of the iodine reservoir. The iodine reservoir is connected to the reactor system by a short piece of high-temperature silicone-rubber tubing. The portion of the iodine train outside the furnace is wrapped with a heating tape and maintained at a temperature higher than the reservoir temperature to prevent iodine from condensing out of the I_2-H_2 mixture.

Phosphine is obtained commercially** as a mixture of either 5 or 10 percent PH_3 in H_2 and is metered directly from a standard cylinder to the reactor system. The flowmeter has been calibrated using the PH_3-H_2 mixtures and using pure hydrogen to compare the experimentally determined flow factor with the calculated flow factor between the two gases to check the dilution factor. Normally a cold trap cooled with a mixture of solid CO_2 and acetone is used to remove water from the PH_3-H_2 mixture.

Yellow phosphorus is obtained commercially*** as 99.999 percent pure and is recrystallized at least once by a sublimation in high-purity hydrogen. Individual charges are used for each experiment and are contained in a break-seal vial which is broken only after it is attached to the reaction system. The phosphorus flow rate is determined by the hydrogen flow rate and the phosphorus temperature. Phosphorus flow rates in the range 0.1 to 1 g/hr are obtained with a hydrogen flow rate of about 20 cm^3/min and at temperatures in the range 200 to 280 C.

Phosphorus trichloride**** was obtained only as cp grade and was given several vacuum distillations prior to use. As in the case of the iodine, a large reservoir of PCl_3 was used for several experiments without refilling. A constant-temperature bath maintained by circulating refrigerated water is used to control the temperature of the PCl_3 reservoir, thus permitting operation in the range 5 to 25 C. This provides PCl_3 flow rates in the range 0.3 to 0.9 cm^3/hr, corresponding to phosphorus flow rates of 0.1 to 0.3 g/hr, with a hydrogen flow rate of about 20 cm^3/hr.

Preparation Procedure and Chemistry

The following is a description of the procedure used for the vapor deposition of AlP in the ceramic reactor. When reading this description, it will be well to have in mind the schematic representation of the vapor-flow system shown in Figure 1 and the reactor system shown in Figure 2. All ceramic parts are baked under an active vacuum better than 10^{-3} torr at a temperature of about 1200 C. After baking for several hours, the system is cooled to room temperature and a flow of argon is maintained through the system while the left end cap is removed and the substrate and aluminum source are loaded into the reactor. After the end cap has been replaced, the system alternately is evacuated and filled with hydrogen several times.

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*Gallard-Schlesinger Chemical Manufacturing Corporation, Garden City, New York.
**Matheson Company, Rutherford, New Jersey.
***The American Agricultural Chemical Company, New York, New York.
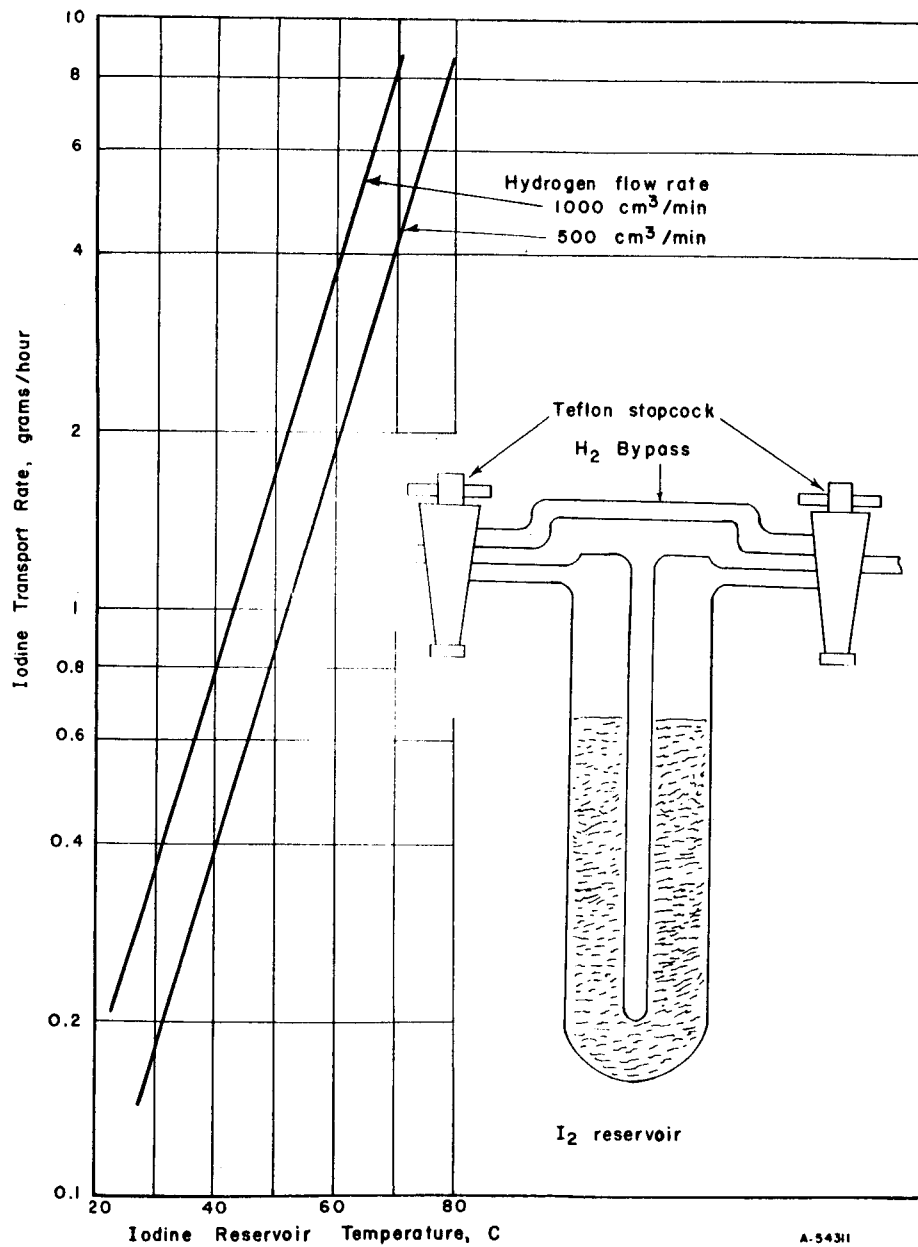****J. T. Baker Chemical Co., Phillipsburgh, New Jersey.

FIGURE 6. IODINE TRANSPORT RATE AS A FUNCTION OF TEMPERATURE
AND SCHEMATIC OF IODINE RESERVOIR

After a final evacuation, the reactor is brought to operating temperature. This is accomplished by regulating the current to each of the two separately wound resistance furnaces. The substrate and aluminum source are brought to temperatures of about 800 C and 1000 C, respectively, under an active vacuum. A hydrogen flow is then started through the system via a bypass arrangement on the iodine reservoir (see Figure 6). When the substrate reaches its final operating temperature and the aluminum source reaches about 1150 C, the hydrogen is directed through the iodine reservoir. Finally, when the aluminum source and iodine reservoir are stabilized at their respective operating temperatures, a flow of the PH_3-H_2 mixture is started.

Vapor deposition is continued for 10 to 20 hours, depending on the deposit thickness desired. Deposition rates have been in the range 10 to 60 μ/hr. After a prescribed deposition time, the I_2 + H_2 flow is changed to pure H_2, the PH_3 + H_2 flow is stopped, and power to the furnaces is shut off. A flow of hydrogen is continued until the reactor system is unloaded.
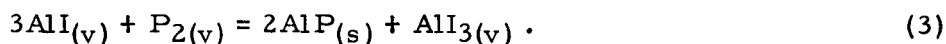
The vapor-deposition scheme was designed to take advantage of the formation of a subiodide of aluminum at the aluminum source, according to the reaction

$$Al_{(1)} + \frac{1}{2} I_{2(v)} = AlI_{(v)} , \tag{1}$$

and the release of free aluminum from the AlI in the substrate region, according to the reaction

$$3AlI = 2Al + AlI_3 \tag{2}$$

or, in the presence of P_2,

$$3AlI_{(v)} + P_{2(v)} = 2AlP_{(s)} + AlI_{3(v)} . \tag{3}$$

The AlP thus formed may be deposited on the substrate. It is noted that the AlI$_3$ remains in the vapor and is deposited outside the furnace region. Figure 7 is a plot of the free energies of formation of several aluminum halides as a function of temperature[3]. It is noted that formation of AlI is favored (relative to that of AlI$_3$) at aluminum-source temperatures above about 1100 C. When the AlI is cooled below 1100 C as it approaches the substrate, the disproportionation shown in Reaction (2) is favored. The free energies of formation of the corresponding chlorides of aluminum are included in Figure 7 for comparison. Aluminum-source temperatures in excess of about 1300 C would be required to utilize this halogen in place of iodine in an analogous reaction scheme.

The formation of AlI at various aluminum-source temperatures has been studied experimentally. Results are shown in Figure 8 in which is plotted (as a function of temperature) the ratio of the number of moles of AlI to the sum of the number of moles of AlI and AlI$_3$ produced with an iodine flow rate in the range 0.7 to 2 g/hr. The distribution of aluminum iodides was obtained assuming that all the iodine was reacted and that the only products were AlI and AlI$_3$. At an aluminum-source temperature of about 1160 C, the product of the aluminum and iodine reaction is nearly 100 percent AlI. The production of AlI decreases rapidly with temperature and is down to 60 to 80 percent in the aluminum-source temperature range 1125 to 1135 C.
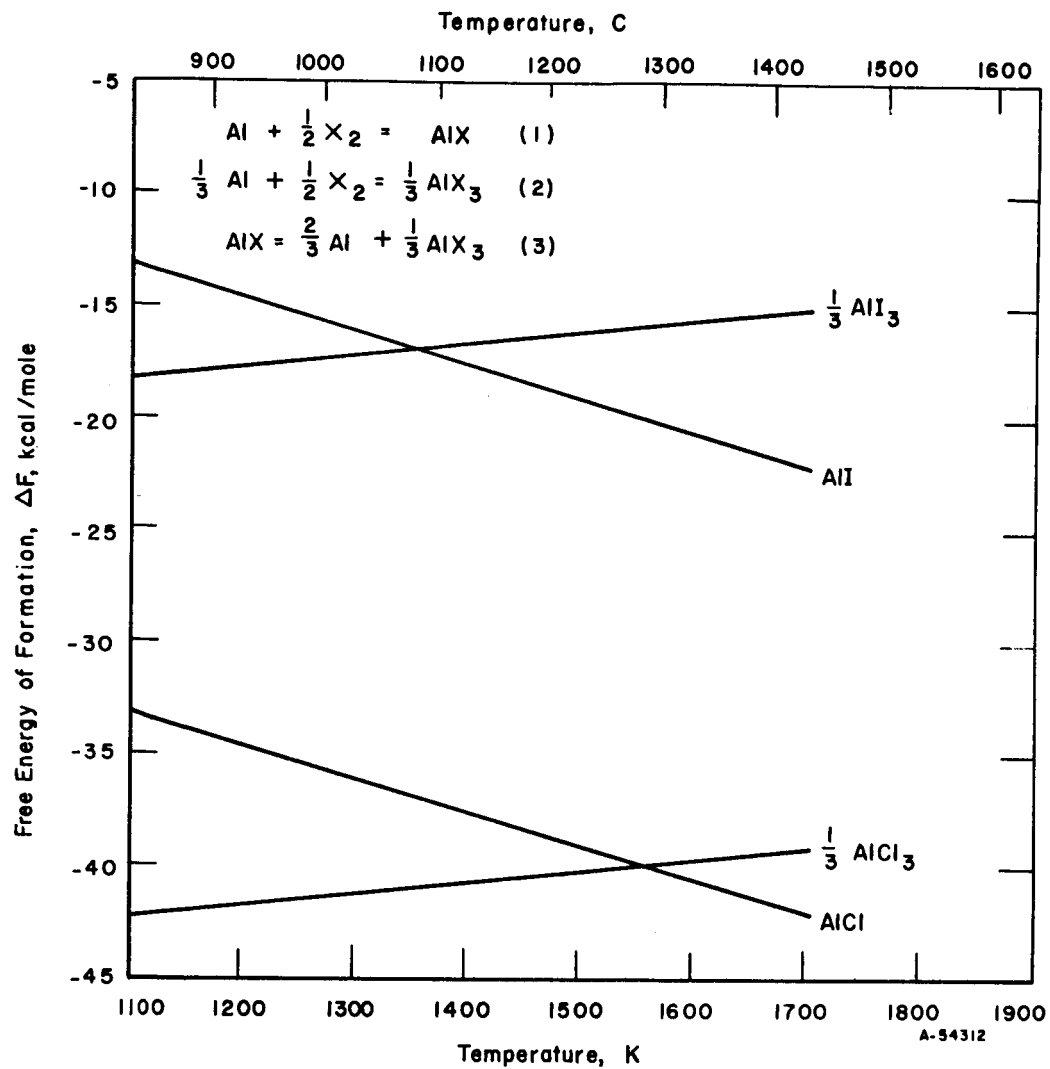
FIGURE 7. FREE ENERGIES OF FORMATION OF ALUMINUM HALIDES
AS FUNCTIONS OF TEMPERATURE
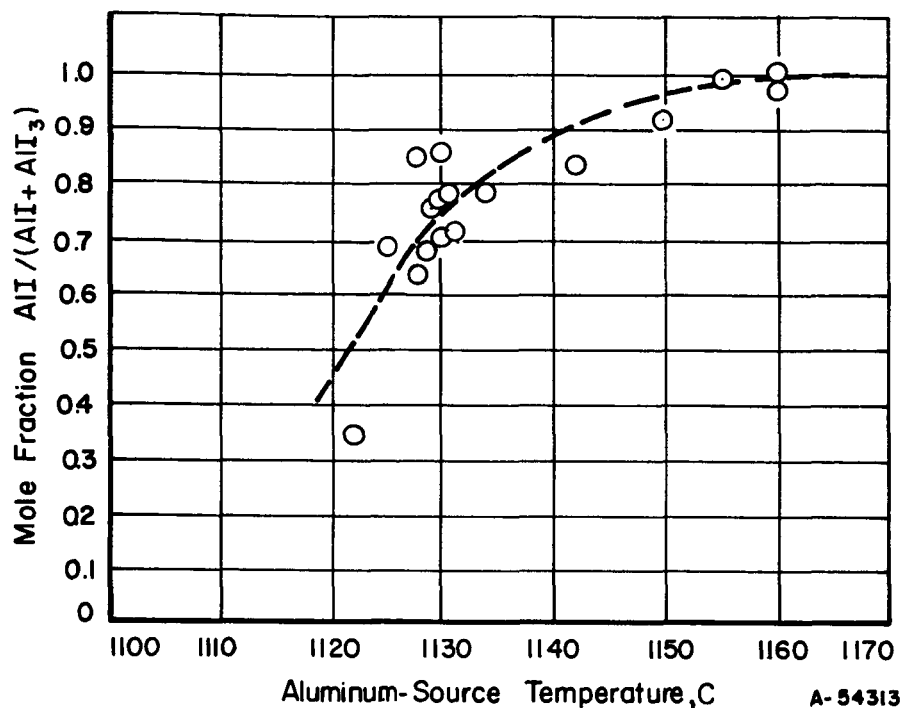
FIGURE 8.   MOLE FRACTION OF AlI PRODUCED BY REACTION OF
ALUMINUM AND IODINE AT VARIOUS ALUMINUM-
SOURCE TEMPERATURES

At higher iodine flow rates, on the order of 5 g/hr, the apparent AlI production usually is less than 50 percent at 1130 C.   This apparent decrease would result if a portion of the iodine is going through the reactor system unreacted at the higher iodine flow rates.   It is advisable to use the higher aluminum-source temperature of about 1160 C and moderate iodine flow rates to achieve the one-to-one relationship between gram atoms of aluminum transported away from the source and the gram atoms of iodine transported from the iodine reservoir.   Hence, the number of gram atoms of free aluminum available to form AlP in the substrate region can be calculated according to Reaction (2), and the number of gram atoms of phosphorus introduced into the reactor system can be selected to yield a variety of aluminum-to-phosphorus atom ratios in the vapor at the point of deposition.

Deposition at low temperatures by the Al-PCl$_3$ process may be represented by Equations (4-a) and (4-b).

$$2Al_{(1)} + PCl_3 \xrightarrow{H_2} Al\text{-}nPCl_3 \text{ complex} \tag{4-a}$$

$$Al\text{-}nPCl_3 \text{ complex} \xrightarrow{H_2} AlP_{(s)} + AlCl_{3(v)} \tag{4-b}$$
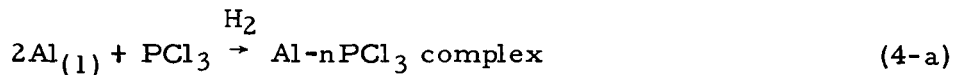
A reaction such as that indicated by (4-a) appears to occur at the Al source.   Hydrogen was used to transport the PCl$_3$ vapor to the aluminum and to transport the complex to the deposition site where AlP was deposited by Reaction (4-b).   The AlCl$_3$ byproduct was transported beyond the substrate zone and deposited on the walls of the reaction tube.

Deposition by the $AlCl_3$-PH_3 process is represented by Reactions (5-a) and (5-b).

$$AlCl_{3(s)} + PH_{3(v)} \xrightarrow{H_2} AlCl_3 - PH_3 \text{ complex} \qquad (5\text{-a})$$

$$AlCl_3 - PH_3 \text{ complex} \xrightarrow{H_2} AlP_{(s)} + 3HCl \qquad (5\text{-b})$$
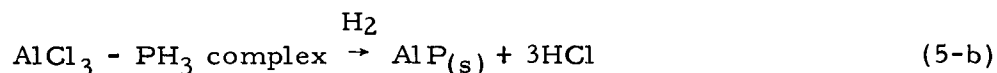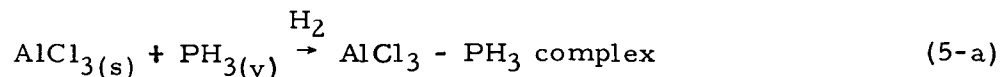
Reaction (5-a) appears to occur at the $AlCl_3$ source. Hydrogen was used to transport the PH_3 vapor to the $AlCl_3$ source and to transport the $AlCl_3$-PH_3 complex to the deposition site where AlP was laid down according to Reaction (5-b). The HCl and unreacted PH_3 were exhausted in the carrier gas. Unreacted $AlCl_3$ was deposited downstream from the substrate.

Charge preparation for Reaction (4) (Al-PCl_3 reaction) involved (1) placing the aluminum contained in an Al_2O_3 boat in the reaction tube as noted in Figure 4 and (2) purging the system with hydrogen. The PCl_3 was transferred under dried argon to the PCl_3 reservoir or bubbler, and the bubbler containing the PCl_3 was attached to the reaction tube. The reaction tube was then purged with dry hydrogen by passing hydrogen through the PCl_3 bypass. The hydrogen was purified by passing it directly from the tank through a palladium purifier and a liquid-air trap.

Deposition of AlP by Reaction (4) was accomplished by (1) heating the aluminum to about 700 C under a hydrogen flow (no PCl_3) and (2) diverting the hydrogen through the PCl_3 bubbler when temperature equilibrium had been established. Hydrogen flow rate was 20 cm^3/min. The PCl_3 reservoir temperature was about 20 C. This corresponds to a vapor pressure of PCl_3 of approximately 125 mm of Hg. Induction heating was used to maintain an aluminum melt temperature of 925-950 C by coupling directly to the Al.

For Reaction (5) ($AlCl_3$-PH_3 reaction), charge preparation was conducted by (1) loading the $AlCl_3$ into a fused-silica boat under argon and transferring the loaded boat to the fused-silica reaction tube which was being purged with argon, (2) assembling the susceptor holder, susceptor, and substrate as noted in Figure 5 and transferring the assembly to the reaction tube, (3) attaching the ground-glass joint to the reaction tube, and (4) replacing argon with hydrogen.

Deposition of AlP by Reaction (5) was conducted by (1) heating the substrate and $AlCl_3$ to the desired temperatures under hydrogen (no PH_3), (2) reverting to the PH_3-H_2 (10 vol %) mixture when temperature equilibrium for the substrate had been reached and the $AlCl_3$ temperature (Zone 1, Figure 5) had reached 75 C, and (3) establishing the desired temperatures in the system for deposition of AlP. PH_3-H_2 flow rates were maintained at 20 to 40 cm^3/min. $AlCl_3$ temperature (Zone 1) was maintained between 120 C and 150 C while Zone 2 was kept normally at temperatures of 400-500 C. The appropriate temperature for the substrate was determined by the substrate material. Silicon substrate temperatures ranged from 750 C to about 1150 C, whereas the temperatures of GaAs substrates were varied from about 650 C to 800 C.

Tantalum was used as the principal susceptor material for deposition of AlP by the $AlCl_3$-PH_3 reaction. These susceptors were disks, approximately 3 cm in diameter and 0.2 to 0.3 cm thick. Other susceptors were graphite (disks approximately 3 cm in

diameter and about 0.6 cm thick) and silicon disks with about the same dimensions. When silicon was used as the susceptor material, it was necessary to preheat it to about 1000 C by coupling to a tantalum disk positioned below the silicon.

Electrical Measurements

Samples for electrical-property studies were obtained from AlP layers grown on silicon substrates and from needles and crystals that were nucleated and grown on the P_2 inlet tube and other parts of the ceramic system. In most cases, the silicon substrates were lapped away leaving the AlP layers. Since AlP reacts violently with water, the lapping is best accomplished under kerosene or with dry abrasive paper in a dry box. Parallelpipeds were cleaved from the layers and used for Hall coefficient (R_H) and resistivity (ρ) measurements. Indium solder contacts were applied either with an ultrasonically agitated soldering tool or a conventional soldering pencil. In the latter case, it was necessary to spark the contacts with a Tesla coil to obtain low-resistance contacts. Measurements were obtained by standard potentiometric techniques using either the standard Hall bar or the Van der Pauw configuration. Voltage drops were measured either with Leeds and Northrup K-3 potentiometer or, in the case of high-impedance samples, a Keithly Model 610-B electrometer.

Current-voltage characteristics of W-AlP point contact diodes were obtained from a Tektronix transistor curve tracer, Type 575. Point-by-point data were also obtained; using a Power Design Incorporated, Model 2005 precision voltage source in conjunction with the Keithly Model 610-B electrometer.

EXPERIMENTAL RESULTS

General Character of Deposits

In general, the experimental preparations yielding the most promising crystal-growth results have been made with the AlI-PH$_3$ system using an aluminum-to-phosphorus ratio greater than unity, a substrate temperature in the range 1120 to 1180 C, and a temperature gradient in the substrate region of about 10 deg/cm. The growth of AlP layers in (111) and (100) silicon substrates was shown to be epitaxial, as determined from the analysis of back-reflection X-ray Laue patterns. A typical pattern obtained from an AlP layer deposited onto {100} silicon is shown in Figure 9. These layers have been 50 to 500 μ thick and some were removed from the substrates prior to the X-ray analysis.

Layers of AlP prepared by the AlI-PH$_3$ reaction, but using lower substrate temperatures (950 to 1050 C) and no temperature gradient in the substrate region, have been polycrystalline. In the past[1], epitaxial layers were produced at temperatures estimated to be as low as 950 C, but in a temperature gradient of about 80 deg/cm. Hence, actual substrate temperatures could have been higher if the substrates were misplaced slightly, or the maintenance of a temperature gradient across the substrate may have been the important difference. At this time, experiments using substrate temperatures >1100 C and no temperature gradient, or experiments using substrate temperatures <1050 C and a moderate temperature gradient have not been attempted for this reaction.

As has been noted, another experimental condition that has an effect on the character of the deposit is the phosphorus-to-aluminum atom ratio present in the vapor and available to form AlP. The procedure used to determine this ratio for comparison purposes is based on the assumption that all of the phosphorus metered into the system is available and that two-thirds of the aluminum transported as AlI is available. Three characteristic groups have been identified in which the individual AlP deposits as members of a group have distinctive physical properties in common.

Depositions at phosphorus-to-aluminum ratios in the range of 3 to 4 appear bright green. Complete coverage of the substrate usually is not attained, and the deposit consists of individual clusters of crystallites. It is noted that at the highly phosphorus rich conditions, clusters of AlP are formed regardless of whether or not water vapor is removed from the PH_3-H_2 mixture. In fact there is no evidence to suggest that the clustering was the result of an oxide layer on the silicon substrate. Depositions at phosphorus-to-aluminum ratios in the range of 1 to 2 appear greenish yellow to dull yellow. The deposits are characterized as uniformly thick deposits that completely cover the substrates. This description holds for deposits made on various substrate materials including silicon, GaP, and GaAs. Depositions at phosphorus-to-aluminum ratios of less than unity appear bright yellow and exceedingly transparent as grown.

The AlP prepared by the Al-PCl_3 reaction was vapor deposited as small needles in the vicinity of the Al melt. (Apparently the complex, Al-nPCl_3, is rather unstable at temperatures of 925-950 C as it was transported for only 2-3 cm.) These needles, shown in Figure 10, were transparent and reddish. Unfortunately the process has not yet been developed to the extent that larger needles or layers of this high-purity AlP can be prepared.

$AlCl_3$ reacts with PH_3 at temperatures less than 100 C to form a PH_3-$AlCl_3$ complex with a P:Al ratio of 1. This complex has a reported melting point of 85 C.[4] It can be vacuum distilled, but it is unstable when heated to higher temperatures. From the experimentation conducted at Battelle, it was determined that the complex could be vapor transported at temperatures of 100 to 150 C and could be decomposed to give AlP at a deposition temperature as low as 650 C. In this case, the AlP was vapor deposited onto the walls of the fused-silica reaction tube.

Continuous layers of AlP (40 to 80 microns thick) were vapor deposited onto GaAs and silicon substrates by the $AlCl_3$-PH_3 reaction. Substrate temperatures were in the range of 650 to 765 C for GaAs substrates and 800 to 1150 C for silicon substrates. $AlCl_3$ (Zone 1, Figure 5) was maintained at a temperature of 100 to 150 C while the Zone 2, Figure 5, was maintained at 400 to 500 C. It is expected that further development of the process will result in thicker layers. The AlP exhibited a yellow to gray color on GaAs substrates and a red to gray color on silicon substrates by reflected light, but was highly transparent in both cases, showing yellow-red color by transmitted light. Visual indication of epitaxy on the GaAs was brought out by etching of the AlP in methanol-H_3PO_4 solution but has not been verified by X-ray analysis.

Uniform mat surface finishes were obtained with the deposits from $AlCl_3$-PH_3 on both GaAs and silicon substrates as shown in Figure 11. It is anticipated that high luster or glossy surface finishes would be obtained for thicker deposits. Variables that may affect smoothness of the deposit are condition of substrate surface prior to deposit, temperature of substrate, rate of deposition, and crystallographic orientation of substrate.
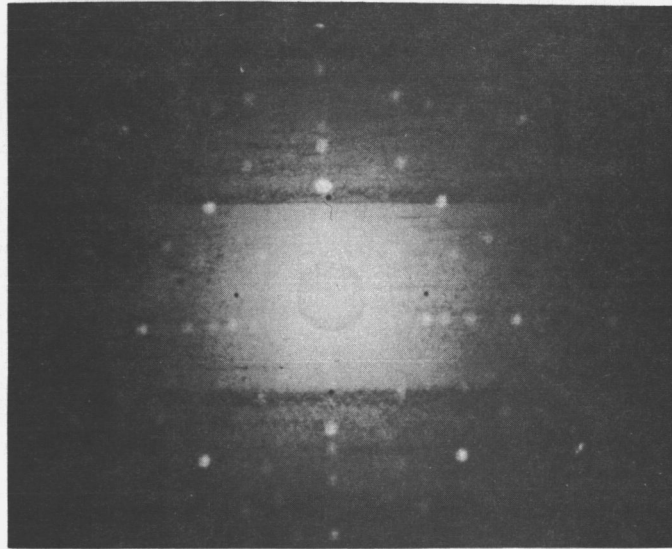
17

FIGURE 9. X-RAY WAVE PATTERN FOR AlP
GROWN ON {100} SILICON

150X

FIGURE 10. AlP NEEDLES PREPARED BY
THE Al-PCl$_3$ PROCESS

Bonding between AlP and GaAs substrates was very good, i.e., the AlP was securely bonded to the GaAs. The AlP-GaAs junction was very clean and distinct as illustrated in Figure 12, which represents a cleaved surface. Good bonding to silicon substrates was obtained only if the oxide film was removed prior to deposition of the AlP.

It has been concluded that GaAs is a suitable substrate material for the vapor deposition of AlP by the PH_3-$AlCl_3$ reaction at temperatures to at least 765 C. The junction formed between the AlP and GaAs at this temperature was very distinct and clean, which indicated that the GaAs is quite stable in such a deposition environment. Silicon may not be a suitable substrate material for deposition of AlP by this reaction. Further study will be necessary. At substrate temperatures of 1125 C to 1150 C, the deposit consisted of a mixture of AlP and silicon. Some deposits consisted of a mixture of re-crystallized (vapor-deposited) silicon needles and AlP needles, whereas others were composed of layers containing AlP intermingled with silicon. At a substrate temperature of 750 C, the deposit did not adhere to the silicon. It is felt that the poor adhesion may have arised from an interfacial oxide layer, and that deposition onto silicon at temperatures near 800 C may be possible if formation of the oxide is prevented. At intermediate temperatures, AlP deposited on silicon was securely bonded to the silicon.

Graphite alone or graphite coated with an inert material, such as boron nitride, may be a suitable susceptor material. High-density graphite has been used as a susceptor material at a temperature of 1100 C without any noticeable attack on the graphite. Tantalum and silicon are not suitable susceptors at temperatures greater than about 1000 C because of attack by the reaction vapors and/or vapor transport of the susceptor material. However, for temperatures up to at least 800 C, tantalum is a suitable susceptor material. No tantalum was detected (emission-spectrographic analysis) in AlP that was deposited directly onto tantalum at about 800 C.

Crystals of AlP examined to date have been chemically stable in dry air but are found to hydrolyze in moist air with the evolution of phosphine and the production of Al_2O_3. Sizable crystals of AlP are much less reactive with moist air than is powder. Also, relatively pure material is less reactive than impure material. The least reactive material prepared to date has been the highest purity single-crystal AlP prepared using a phosphorus-to-aluminum ratio of less than unity in the vapor phase. Such crystals were still intact and usable after an exposure of 24 hours to ambient air at approximately 50 percent relative humidity. For comparison, impure powdered AlP would be completely reduced to Al_2O_3 in a matter of a few minutes when exposed to the same conditions.

Impurity Content and Electrical Properties

Silicon is the major impurity found by emission-spectrographic analysis, in AlP crystals prepared in the subject research. Since the AlP is found to be n-type with carrier concentrations usually on the same order as the silicon concentration, it appears that silicon enters the AlP substitutionally on the aluminum sublattice, acting as a donor impurity. This is similar to the usual behavior of silicon in GaAs, GaP, and InP.

150X

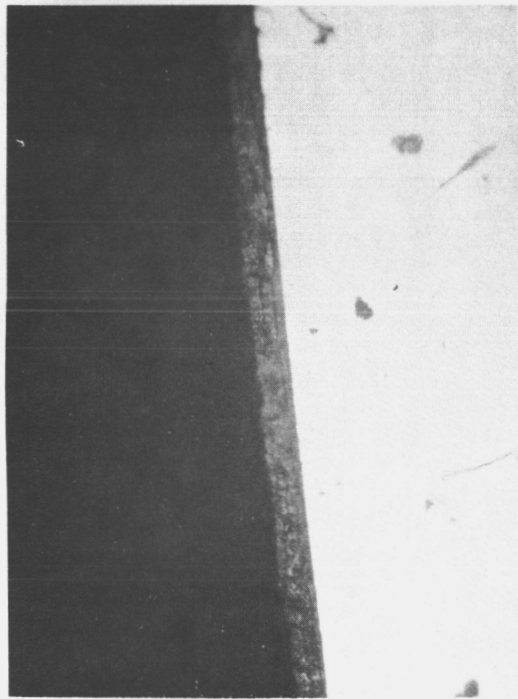FIGURE 11. AlP DEPOSITED ON GaAs
BY THE $AlCl_3$-PH_3 PROCESS

150X   AlP   GaAs

FIGURE 12. AlP-GaAs INTERFACE FOR
DEPOSIT PREPARED BY THE
$AlCl_3$-PH_3 PROCESS

Table I is a compilation of the silicon content and free-electron concentrations for AlP samples prepared under various conditions, primarily in the ceramic reactor system. The free-electron concentration, n, was determined from Hall-effect measurements at room temperature, assuming $n = 1/R_H e$, where R_H is the Hall coefficient and e is the charge on an electron. The silicon concentration is expressed in ppm (atomic) and by the number of silicon atoms per cubic centimeter. (Crystalline AlP contains approximately 5×10^{22} atoms/cm^3.) Not only were the silicon contents high in AlP samples prepared in a quartz reactor, but also the copper concentrations in the AlP were relatively large, e.g., AlP from the quartz reactor (see Experiment 2) contained 50 ppm (atomic) copper as compared with AlP from the ceramic reactor (all other experiments shown) which contained approximately 2 ppm (atomic) copper.

GaP and GaAs substrates were substituted for the silicon substrates in the ceramic system to determine whether or not the AlP was being contaminated with silicon from the substrate. It does not appear that such contamination occurs to a significant extent under the experimental conditions used and at the present level of contamination. The first layers of AlP prepared using PH_3 exhibited moderately large resistivities (>100 ohm-cm) and low carrier concentrations, e.g., see Experiment 28 in Table I. It is noted, however, that these layers contained about 50 ppm silicon as determined by emission-spectrographic analysis. After a few experiments produced similar results, a cold trap at about -73 C was placed in the PH_3 vapor train to remove any water vapor that might be present and serve as a source of oxygen. This addition to the system was suggested to improve crystal-growth conditions by preventing an oxide from forming on the substrate. An appreciable amount of H_2O was collected during each experiment with the cold trap present. The subsequently produced layers exhibited electrical properties commensurate with their respective silicon contents, e.g., see Experiment 52, 62, 95, and 97 in Table I. All experiments in which a cold trap was not present in the PH_3 vapor train have produced relatively high-resistivity AlP.

TABLE I
SILICON CONCENTRATIONS IN SELECTED SAMPLES OF AlP PREPARED
BY THE AlI-PH$_3$ PROCESS

Experiment	Substrate Temperature, C	Substrate Material	Silicon Content, ppm	Silicon Content, atoms/cm^3	Free-Electron Concentration, cm^{-3}
2[a]	1000	Si	1000	5.0×10^{19}	5.5×10^{19}
49	1020	Si	--	--	1.8×10^{19}
52	1010	GaP	500	2.5×10^{19}	2.0×10^{19}
62	980	GaAs	30	1.5×10^{18}	1.4×10^{18}
95	1120	Si	40	2.0×10^{18}	1.3×10^{18}
97	1150	Si	40	2.0×10^{18}	1.4×10^{18}
28[b]	960	Si	50	2.5×10^{18}	$<10^{15}$

(a) Reactor material was quartz throughout for Experiment 2. In all other experiments shown, ceramic parts were used.
(b) The cold trap in the PH_3 vapor train (see Figure 1) was not present in this experiment.

It appears, therefore, that the inclusion of oxygen during the growth of AlP has an effect on the electrical properties of the resulting layers. The effect is similar to that described by Reid, Baxter, and Miller[5] in the case of work on GaAs in which it appeared that oxygen combined with silicon to mask it as an electrically active impurity. Crystals of GaAs growth with oxygen present could contain as much as 10 ppm silicon and yet have carrier concentrations of less than 1×10^{16} cm^{-3} and electron mobilities of greater than 6000 cm^2/volt-sec.

Table II is a compilation of the electrical properties of selected samples of AlP. All samples prepared to date have been n-type, hence the mobility values quoted are for electrons. Among the samples shown in Table II are examples representative of preparations involving vapors containing phosphorus-to-aluminum atom ratios in the range 0.5 to 2, of monocrystalline as opposed to polycrystalline material, and of epitaxial layers as opposed to needles. It is noted that Sample 97 exhibits the best combination of carrier concentration (1.4×10^{18} cm^{-3}) and mobility (80 cm^2/volt-sec) achieved to date with the AlI-PH$_3$ process. This material was grown at about 1150 C using a phosphorus-to-aluminum ratio of about 0.6. Sample 107 has a lower carrier concentration (4.5×10^{17} cm^{-3}), but, the low electron-mobility value (5 cm^2/volt-sec) suggests the possibility that the low carrier concentration was achieved by impurity compensation rather than by impurity removal.

The AlP prepared by the Al-PCl$_3$, low-temperature process deposited as small needles in the vicinity of the aluminum melt. None of these needles was large enough to permit evaluation of the electrical properties. However, spectrographic determinations of silicon content were obtained and the results are given in Table III. The results listed in Table III indicate that the choice of boat material used to contain the aluminum melt can have a significant influence on the level of silicon contamination. The graphite boat of Experiment A for example was known to contain silicon at the 30 ppm level. Use of an Al$_2$O$_3$ crucible (Experiment B) of a quality similar to that used in the all-ceramic reactor suppressed the silicon content from 100 ppm to 50 ppm, a value comparable to that obtained with the ceramic system. In other words, even with a quartz liner, the Al-PCl$_3$ system produced material comparable in purity to that obtained in the higher temperature all-ceramic system. It is not surprising then that Experiment C, which employed a Lucalox boat and liner, yielded AlP containing the lowest observed silicon content (10 ppm). This is particularly encouraging since the PCl$_3$ used was reagent grade and is felt to be itself a source of silicon.

Purity of the AlP deposited by the PH$_3$-AlCl$_3$ reaction was not as high as the purity of that deposited by the Al-PCl$_3$ reaction, probably because high-purity reactants were not used in the preparation. High-purity AlCl$_3$ was not available commercially. As purchased, the AlCl$_3$ contained 30 ppm silicon, and AlP deposited by this reaction contained about 300 ppm silicon. It was possible to deposit AlP layers by the PH$_3$-AlCl$_3$ process, however, and electrical evaluations of two of these layers were obtained. In one experiment, an approximately 40 μ thick film was deposited onto a silicon substrate. Electrical measurements on samples taken from various parts of the deposit, with the film still on the substrate, yielded typical values of electron concentration of about 2×10^{17} cm^{-3} with corresponding electron mobility of about 25 cm^2/v-sec. One such measurement yielded values of electron density and electron mobility of 3.5×10^{16} cm^{-3} and 98 cm^2/v-sec, respectively. The other layer grown by the low-temperature process on which electrical data were obtained was one deposited onto silicon at a relatively low substrate temperature and which did not adhere to the substrate. This layer was polycrystalline and was of relatively high resistivity, ~500 ohm-cm.

TABLE II
ELECTRICAL PROPERTIES OF AlP SAMPLES PREPARED
BY THE All-PH_3 PROCESS

Sample	Temperature of Measurement, K	Resistivity, ohm-cm	Electron Mobility, cm^2/volt-sec	Carrier Concentration, cm^{-3}
1	298	0.0032	60	3.1×10^{19}
2	298	0.0044	26	5.5×10^{19}
3	298	0.044	9	1.6×10^{19}
49	298	0.018	19	1.8×10^{19}
52	298	0.0085	36	2.0×10^{19}
62	298	0.405	11	1.4×10^{18}
95(b)	298	0.0654	75	1.3×10^{18}
	77	0.304	30	6.8×10^{17}
97(b)	298	0.0555	80	1.4×10^{18}
	77	0.455	31	4.5×10^{17}
107(b)	298	2.68	5	4.5×10^{17}
110A(b)	298	0.0246	41	6.2×10^{18}
110B	298	0.0416	33	4.5×10^{18}
113(b)	298	0.0661	23	4.1×10^{18}
118(b)	298	0.0704	50	1.8×10^{18}
104(a, b)	298	360	--	--
121(a)	298	250	--	--
28(a)	298	500	--	$<1 \times 10^{15}$
	350	210	--	--
	400	100	--	--

(a) The cold trap in the PH_3 vapor train (see Figure 1) was not present when this sample was prepared.
(b) Needle specimens.

TABLE III
SILICON CONCENTRATIONS IN AlP PREPARED BY
THE Al-PCl₃ PROCESS

Experiment	Boat	Liner	Silicon Content, ppm
A	Graphite	None	100
B	Al_2O_3 (99.7% pure)	Quartz	50
C	Lucalox	Lucalox	10

Device Studies

Initial device studies were carried out on tungsten-AlP point-contact diodes using low-resistivity AlP from Depositions 110 and 118 ($n = 4.5 \times 10^{18}$ and 1.8×10^{18} cm^{-3}, respectively). Because of the relatively high carrier concentrations, the devices are essentially Schottky barrier devices. That is, they are majority carrier devices and do not provide a source of information on minority carrier lifetimes, injection, etc. Nevertheless, they are readily fabricated and may be used to provide useful information about the electrical and chemical stability at elevated temperatures and under thermal cycling.

The diodes employed a back contact of indium applied with an ultrasonic soldering gun. The rectifying contact consisted of an 8-mil-diameter tungsten wire, electrolytically etched to a fine point, which was then brought into contact with the freshly lapped AlP surface.

In some cases, it was necessary to apply a relatively high forward bias > 20 v before conduction was observed. Once the "critical" bias (which varied from sample to sample) was reached, low voltage rectifying characteristics similar to those shown in Figures 13-18 were observed. (When conduction was established, the majority of the applied voltage appeared across a current limiting resistor in series with the device.) The large applied bias was apparently necessary to break through an oxide or other foreign layer immediately beneath the point contact.

In cases where rectifying contact characteristics were observed immediately upon application of low bias, the forward conductance was usually low. The forward characteristics could be improved by forcing a relatively large pulse of forward current (~50 ma) through the device, i.e., by "forming" the contact. Although forming point contacts can cause the formation of a p-n junction by alloying or impurity diffusion from the whisker into the semiconductor, it is not felt that p-n junction formation resulted in this case. In view of the high doping levels in the substrate, the relatively low peak of current pulses used, and the inability to produce a p-n junction by diffusion, it is felt that the forming operation served merely to establish an intimate metal-semiconductor contact.

Room-temperature I-V characteristics were obtained both with the diode in the dark and under illumination. No differences in characteristics were observed upon illumination.

Typical room-temperature I-V curves for diodes prepared from AlP layer Number 110 are shown in Figures 13 and 14. The diodes labelled 110-1 and 110-2 were obtained from the same AlP wafer by positioning the tungsten point at two different locations. Figure 13 shows the entire I-V curve in the upper trace and an expanded curve of the forward characteristic in the lower trace. These curves were obtained after the point contact had been formed by passing forward currents of ≤50 ma for a few seconds. The two curves shown in the upper trace for Figure 14 show the effect of forming on the forward characteristics. Still referring to the upper trace, the lower curve was obtained prior to forming and the upper curve after forming. The increased conductance effected by forming is evident. The lower trace in Figure 14 shows the entire I-V curve after forming.
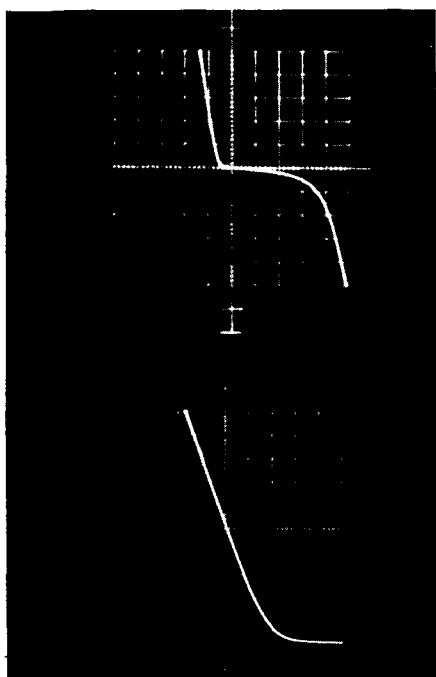
Upper trace:

    1 ma/div vertical
    1 v/div horizontal

Lower trace:

    Forward characteristics

        0.5 ma/div vertical
        0.2 v/div horizontal

Note: Origin of lower trace is lower right-hand corner.

FIGURE 13. ROOM-TEMPERATURE I-V CHARACTERISTICS OF DIODE 110-1

It may be noted that although there is no well-defined breakdown for either diode, the better reverse characteristics are exhibited by Diode 110-2 (note scale change between Figures 13 and 14). Similarly, Diode 110-2, after forming, has a higher forward conductance. The differences in the characteristics of Diodes 110-1 and 110-2, are probably due either to variations in the forming operation or to lateral variations in the surface properties of the lapped AlP layer.

To obtain diode characteristics as a function of temperature, a high-temperature holder was constructed of lavite. Diode I-V characteristics up to 1000 C were measured with this holder. A Chromel-Alumel thermocouple located in the vicinity of the point contact was used as a temperature sensor.

In the initial temperature run, the current-voltage characteristics of Tungsten-AlP Diode 118 were obtained at various temperatures of 25 C to 500 C. The diode was fabricated from a 0.4 x 0.3 x 0.05-cm die from AlP Deposition 118 (n = 1.80 x 10^{18} cm^{-3}). One surface of the die was indium coated with an ultrasonic soldering tool.

The die in turn was soldered to a stainless steel pin. An exposed surface of the AlP was then lapped on crocus cloth, and the die and pin were loaded into a lavite holder so that the lapped surface contacted the tungsten whisker. The lapping and loading were done in an argon atmosphere. The assembled structure was then placed in a quartz tube. A fore pump maintained an active vacuum inside the quartz during measurement of diode properties.

The variation of forward current with increasing temperature during initial heating was anomalous in that the forward conductance was relatively constant below about 300 C and actually decreased at higher temperatures. However, by forming the contact at 494 C, significant improvement in both the forward and reverse characteristics was obtained. The characteristics at 494 C are shown in Figure 15. The diode was subsequently reheated and d-c I-V data obtained at 25, 108, 217, and 329 C. These data in Figures 16 and 17 show the forward and reverse characteristics, respectively. The solid curves in Figure 16 have been obtained by correcting the forward voltage for series resistance, i.e., $V = V_a - IR_s$, where V_a is the applied bias, R_s is the series resistance required to linearize the plot at high voltage (>0.4 V), and I is the measured diode current. V, then, is the actual voltage appearing across the barrier. The values of R_s required to achieve data linearization were 135 Ω for the 25 C data and about 90 Ω for the remaining data. The resulting straight lines can be described by the equation I = $I_o [\exp (qV/\eta kT) - 1]$.

Even after correcting for series resistance, however, the experimental data deviate from the simple diode equation in several respects. First, the values of η calculated from the linear portions of the forward characteristics are all greater than unity; they vary from 1.51 at 25 C to 1.20 at 329 C. Second, there is an excess current at low biases. This excess current becomes less important with increasing temperature and is not in evidence in the 329 C data. Third, the reverse current does not saturate, but rather exhibits an exponential dependence on voltage.

In view of the present inability to etch and clean AlP chemically, the discrepancies may be attributed tentatively to surface effects (e.g., the multicontact effect[6]. As a result, it would be premature to attempt a detailed analysis of the data at this time. It is encouraging, however, that, in spite of large forward series resistance and high reverse-leakage currents, a rectification ratio of > 100 is obtained at 1-volt applied bias at a temperature of 329 C and that some rectification still occurs at 500 C.

To determine the effects of high temperature and of thermal cycling on diode characteristics, Diode 118-2 was heated to 1000 C at a heating rate of about 200 degrees per hour, held at 1000 C for 1 hour, and subsequently cooled to room temperature. The I-V data for 25 C before and after this temperature excursion are shown in Figure 18. It may be seen from the figure that no appreciable change occurred in the I-V characteristics.
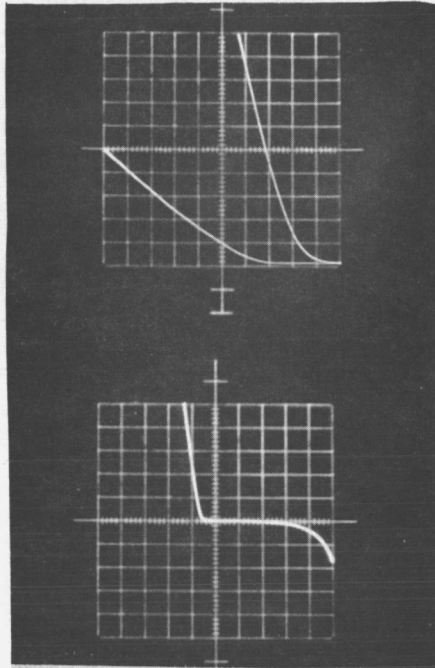
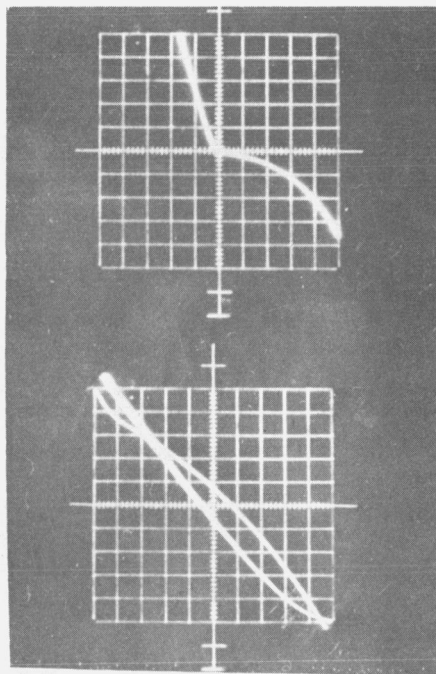Upper trace:

   Forward characteristics

      0. 5 ma/div vertical
      0. 2 v/div horizontal

      Lower curve - before forming
      Upper curve - after forming

Lower trace: 2 ma/div vertical
                 1 v/div horizontal

Note: Origin of upper trace is
        lower right-hand corner.

FIGURE 14.   ROOM-TEMPERATURE I-V CHARACTERISTICS OF DIODE 110-2

Upper trace: 2 ma/div vertical
                 1 v/div horizontal

Lower trace:

   Forward characteristics

      1 ma/div vertical
      0. 2 v/div horizontal

   Reverse characteristics

      0. 1 ma/div vertical
      0. 2 v/div horizontal

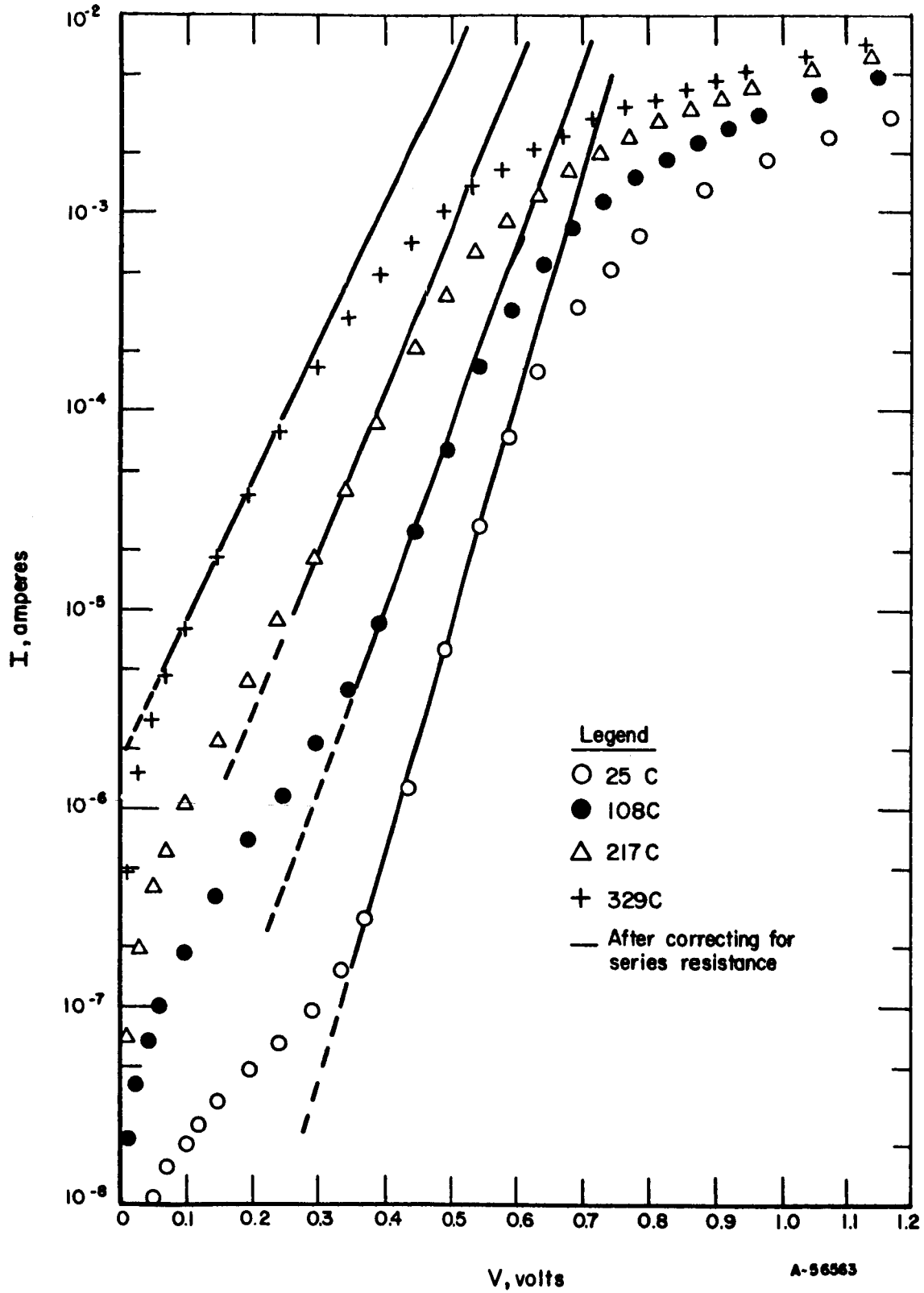FIGURE 15. I-V CHARACTERISTICS OF DIODE 118 AT 494 C

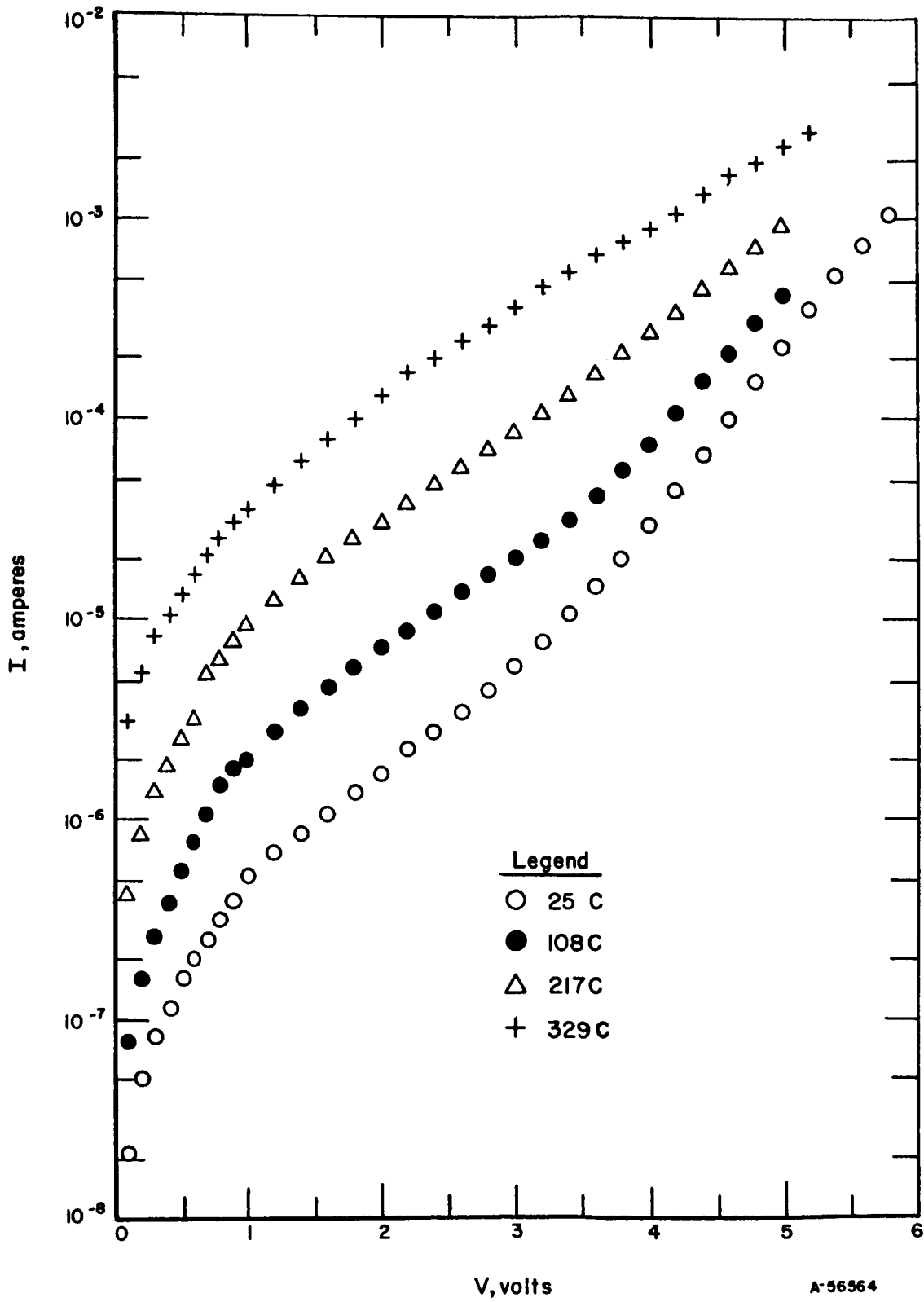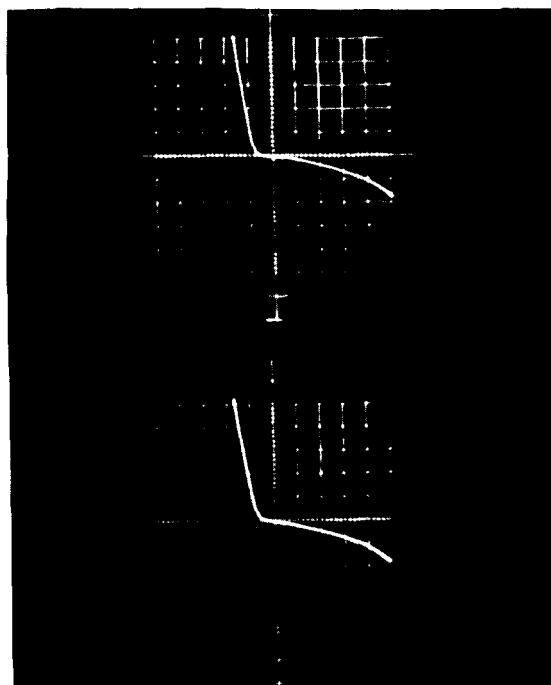FIGURE 16. FORWARD CHARACTERISTICS OF DIODE 118
AT VARIOUS TEMPERATURES

FIGURE 17. REVERSE CHARACTERISTICS OF DIODE 118
AT VARIOUS TEMPERATURES

Upper and lower traces:

2 ma/div vertical
1 v/div horizontal

Upper trace - before anneal
Lower trace - after anneal

FIGURE 18. ROOM-TEMPERATURE CHARACTERISTICS OF DIODE 110-3
BEFORE AND AFTER 1000 C ANNEAL

Diffusion Studies

Attempts to form p-n junctions by diffusion of the p-type dopant, zinc, into n-type
AlP wafers (sans substrates) were relatively unsuccessful. Two different methods were
attempted. In the first method, a two-zone technique was employed. The AlP wafers
and zinc source were sealed in opposite ends of a 30-cm-long, evacuated quartz tube
(13-mm ID). The tube was then placed in a two-zone furnace with the zinc at 720 C and
the AlP at 1130 C for 10 days. At the end of this period, it appeared that all of the AlP
had been transported from the 1130 C zone and deposited in a narrow band on the wall of
the quartz tube. The temperature at which the deposition took place is estimated as
~1050 C. Severe devitrification of the quartz that also was observed suggested that the
AlP was transported by oxygen, which entered through the wall of the damaged quartz.

To circumvent the AlP transport problem, the two-zone method was abandoned in
favor of a single-zone (isothermal) technique. In this case the zinc and AlP wafers from
Runs 28 and 62 (n = 1.4 x 10^{18} cm^{-3}) were sealed in a 5-cm x 9-mm-ID, evacuated
quartz ampoule. The entire ampoule was maintained at 1130 C for 90 hours. A larger
diameter section of quartz tubing also was used as a furnace liner to help prevent devit-
rification of the ampoule. With this technique, the ampoule and the AlP wafers were in-
tact at the end of the diffusion. Attempts to locate a p-n junction by means of thermal
probing, sheet resistivity measurements, and the polarity of point contact rectification
were unsuccessful, probably because of the high impedance levels encountered. The
wafers appeared to have high resistivity throughout. Hall elements were fabricated, but
the high impedance levels (sample resistance plus contact resistance $\geq 10^{13}$ Ω) precluded
determination of R_H or ρ. The samples, being opaque and exhibiting photoconductivity,

indicated that an appreciable portion of the total-sample resistance was due to a high AlP bulk resistivity. It appears from this that compensation did occur through the incorporation of a p-type impurity and that p-n junction formation by diffusion techniques may be possible.

ANALYSIS OF RESULTS AND RECOMMENDATIONS

The results obtained with the AlI-PH$_3$ system demonstrated that a significant improvement in the quality of AlP layers can be achieved by elimination of quartz components from the high-temperature regions of the CVD reactor. However, the electrical properties and spectrographic analyses of the material indicate that the level of silicon contamination is still far too high to permit a thorough assessment of the device potential of AlP. It appears that, with the ceramic systems, higher quality ceramic components will be required to achieve further significant improvement in the purity of the deposits.

The results obtained with the low-temperature deposition processes initiated in the subject program offer a reasonable alternative approach. However, these experiments were of a preliminary nature and much remains to be learned before the low-temperature processes can be fully exploited. For example, the exact compositions of the complexes are as yet unknown, and the optimum temperatures for transporting and dissociating the complexes are yet to be determined. In addition, schemes for further purification of starting materials must be devised. (This is also probably true for the ceramic system.) The advantages of the low-temperature approach, however, would appear to justify its pursuit.

Insofar as device potential is concerned, it has already been suggested that the present purity of AlP is probably not sufficient to permit an accurate prediction of optimum behavior. On the other hand, as a result of the advances made under this program, a means is now available for producing materials of sufficiently improved purity that more detailed characterization of AlP may be undertaken. Such characterization should, of course, include not only measurements of transport properties but also optical studies. The limited device studies made under this contract suggest that AlP can withstand thermal cycling to high temperatures without undergoing drastic chemical or physical changes. Although the diffusion experiments were inclusive in establishing the feasibility of fabricating p-n junctions by diffusion techniques, the prospects of preparing planar p-n junction structures by incorporation of a p-type impurity during vapor growth appear good. The remaining problems to be solved are not unique to AlP but rather are characteristic of high band gap semiconductors in general. In view of the relatively small amount of effort expended on AlP in comparison with some of the more well-known candidate materials for high-temperature devices, the results of this investigation are considered to be encouraging. Active pursuit of the further development of AlP is strongly recommended.

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NEW TECHNOLOGY APPENDIX

After a diligent review of the work performed under this contract, it is concluded that no innovation, discovery, improvement, or invention was made.

RDB:EPS:FJR/jvd