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HIGH-TEMPERATURE-MATERIALS STUDY

By F. J. Reid, S. E. Miller, and R. D. Baxter

June 1967

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HIGH-TEMPERATURE-MATERIALS STUDY

By F. J. Reid, S. E. Miller, and R. D. Baxter

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SUMMARY

Aluminum phosphide, AlP, was grown by a chemical vapor-deposition process on single-crystal substrates of {111} silicon, {100} silicon, GaP, and GaAs at substrate temperatures in the range 950 to 1200 C. An understanding was obtained of various chemical reactions of importance to the development of the vapor deposition of AlP, including reactions of aluminum and iodine, PCl_3 and AlI, P_2 and AlI, and AlP and iodine. In the process involving AlI and PH_3, vapor flows representative of phosphorus-to-aluminum atom ratios in the range 0.5 to 4 were used. Mass-transport rate and vapor velocity also were considered in the vapor-growth studies. However, substrate temperature, temperature gradient at the substrate, and phosphorus-to-aluminum atom ratio appeared to be the more important considerations in achieving epitaxial deposits of AlP on the single-crystal substrates. Epitaxial deposits of AlP up to 600 microns thick have been grown on silicon substrates at about 1120 C in a temperature gradient of about 10 deg/cm.

A vapor-growth reactor system containing only ceramic parts in the high-temperature regions of the system was designed and put into operation during this program. The deposits of AlP grown in this system consistently contained lower concentrations of impurities than did the deposits grown in a system containing quartz parts. The AlP has been characterized by emission-spectrographic analyses and by electrical-properties studies. It has been apparent that the inclusion of oxygen during a preparation has an effect on the electrical properties of the resulting AlP layer. High-resistivity (>100 ohm-cm) material has been prepared by the addition of oxygen. In general, the AlP contains free-electron concentrations on the order of $1 \times 10^{18}/cm^{-3}$, and electron mobilities as large as 80 $cm^2/$volt-sec have been obtained. This is the best combination of carrier concentration and mobility ever reported for AlP.

INTRODUCTION

The objective of the research program is to provide knowledge useful for producing electronic devices that can be operated at higher temperatures (>500 C) than is possible with currently available devices. The material under investigation is the III-V compound semiconductor, AlP; vapor-phase growth techniques are being studied for producing single crystals of the material. AlP has a melting temperature in excess of 2000 C and a forbidden band gap of approximately 2.5 ev, which is the largest band gap achievable in a III-V compound semiconductor that can be prepared readily in a zinc-blende crystal structure.

A material for electronic devices capable of operating at high temperatures must possess a wide forbidden band gap such that the concentration of intrinsic carriers activated at the operating temperature is small compared with the controlled concentrations of extrinsic carriers. In addition, the material must exhibit a low vapor pressure and low dissociation pressure at the operating temperature. Finally, the material must be amenable to preparation in a pure, single-crystal form and to fabrication of p-n junctions. Such properties are to be found among the compound semiconductors, where the III-V compounds are promising materials.

The III-V compound semiconductor AlP has received little attention in the past, while various others of this family have been studied extensively and characterized reasonably well. This situation is understandable when it is realized that AlP has a melting point in excess of 2000 C and a dissociation pressure of tens of atmospheres at its melting point. Preparation of AlP utilizing vapor-phase reactions gives relief from the high melting temperatures and pressures. This technique has the advantages that crystal growth takes place well below the melting temperature and epitaxial growth may be achieved on substrates of lower melting compounds or elemental semiconductors. In addition, this technique is the one involved in the versatile epitaxial-device techniques being applied today. It is noted that AlP is a compound that is isoelectronic with the most useful of the Group IV elemental semiconductors, silicon. Other III-V compounds, which are isoelectronic to Group IV semiconductors, are GaAs and InSb — two compounds that are by far the most interesting and potentially useful of the family in their respective band-gap ranges.

PRIOR WORK ON ALUMINUM PHOSPHIDE

A review of the literature on the subject of the preparation of AlP up to 1944 is given by White and Bushey (Ref. 1). Early work indicated the existence of several compounds of aluminum and phosphorus, such as Al_3P_5, Al_7P_3, Al_5P_3, and Al_3P; however, these authors contend that there is only one compound, AlP, which has the zinc-blende structure. Rabenau (Ref. 2) has continued the review up to 1960, which includes preparation of AlP by reacting fine-grained aluminum powder or liquid aluminum with red phosphorus or phosphorus vapor at temperatures in the range 500 to 1500 C and by crystallizing AlP from liquid zinc saturated with aluminum and phosphorus.

In reactions involving powdered aluminum, the product obtained is a slightly sintered, powdery mass containing, in addition to the compound AlP, large amounts of free aluminum, Al_2O_3, and $AlPO_4$. Upon reacting molten aluminum with phosphorus vapor, the product obtained is either pulverized, in a state similar to the product mentioned above, or is in the form of small crystals of AlP imbedded in a matrix of aluminum from which the AlP crystals must be tediously removed by mechanical or chemical means. The crystallization from liquid zinc is difficult to carry out because extremely slow crystallization rates must be maintained, and the resulting AlP is subject to contamination by zinc.

Since 1960, chemical-vapor-deposition techniques have become widely used to prepare epitaxial layers of silicon, germanium, and the III-V compound semiconductors. In addition to Battelle work, initiated in 1964 with the resulting publication by Reid, Miller, and Goering (Ref. 3), the use of vapor-deposition techniques for the preparation of AlP has been reported by Bolger and Barry (Ref. 4) and Richman (Ref. 5).

Lattice-constant determinations have yielded values for AlP of 5.4625 ± 0.0005 A (Ref. 5), 5.467 ± 0.002 A (Ref. 6), 5.462 A (Ref. 7), and 5.451 A (Refs. 1 and 8). Values of the room-temperature optical band gap of AlP have been reported to be 2.42 ev (Ref. 9), 2.45 ev (Ref. 5), and 3.0 ev.* Electroluminescence, photoluminescence, and photoconductivity have been observed with AlP crystals (Ref. 9). However, in general, very little has been reported on the electrical properties of AlP.

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*This value of 3 ev has been quoted for some years; however, it has not been possible to trace the value back to an original reference. The value is quoted in two different chapters of Hannay's book Semiconductors, Reinhold Publishing Corporation, 1959.

The vaporization behavior of AlP has been studied by a Knudsen-cell-mass-spectrometric technique (Ref. 10). In this work, the gaseous AlP molecule was first detected at about 1400 C. The equilibrium partial pressures of $AlP_{(g)}$, $Al_{(g)}$, and $P_{2(g)}$ at this temperature were 2.4×10^{-6}, 2.8×10^{-1}, and 9×10^{-2} mm of Hg, respectively. At about 1530 C, the respective partial pressures were 1.4×10^{-5}, 1.3, and 2.0×10^{-1} mm of Hg.


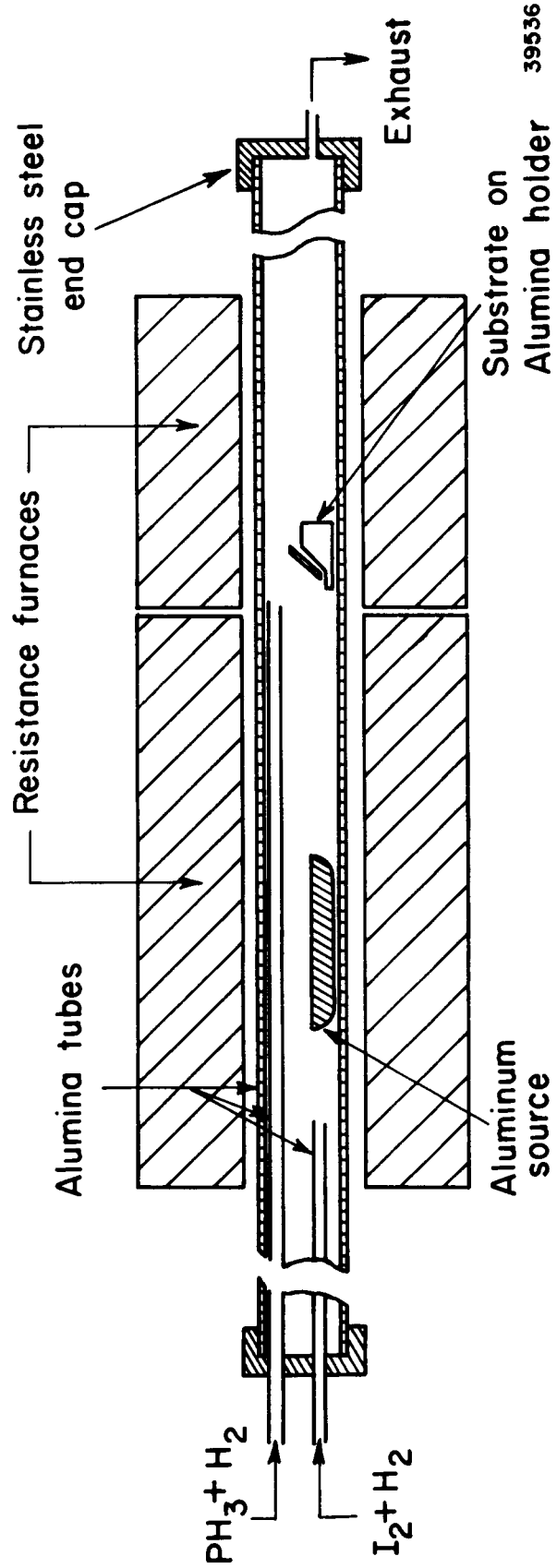## EXPERIMENTAL DETAILS

Vapor Flow System

Figure 1 is an illustration of the important features of the vapor-flow system being used in the preparation of AlP. The chemical reactions that appear to occur in the various temperature zones are indicated. Throughout the high-temperature zones labeled T_2 and T_3, only ceramic parts are used to hold the molten aluminum source and the substrate and to contain the vapor flow. The use of ceramic parts was introduced to eliminate quartz parts that were etched at the high temperature by the corrosive vapors, thus providing a source of silicon as a contaminant to the AlP.

The PH_3, diluted with hydrogen, is supplied to the system from a compressed-gas cylinder. The cold trap shown in Figure 1 in the PH_3 vapor train was added to remove water from the commercial source of PH_3. An elemental phosphorus source can be substituted for the PH_3 source by replacing the cylinder with a phosphorus reservoir through which hydrogen gas is passed. The reservoir is held at a specific temperature to provide a given phosphorus flow rate into the system. The use of elemental phosphorus with the ceramic system has a drawback in that it is difficult to connect the phosphorus reservoir to the ceramic parts and still maintain the phosphorus vapor at the reservoir temperature. Similarly, PCl_3 can serve as the source of phosphorus instead of the PH_3. However, with the PCl_3 source, close control of the PCl_3-to-AlI ratio in the substrate region must be maintained, else $AlCl_3$ is formed at the expense of AlP formation.

Figure 2 shows the details of the high-temperature zones (labeled T_2 and T_3 in Figure 1) of the reactor system. All parts within these zones are made of alumina (Al_2O_3) and include the reaction tube, inlet tubes for the introduction of iodine and phosphorus, the aluminum source boat, and the substrate holder. The predominant vapor flow is from left to right, with the iodine being brought into the system by maintaining a constant
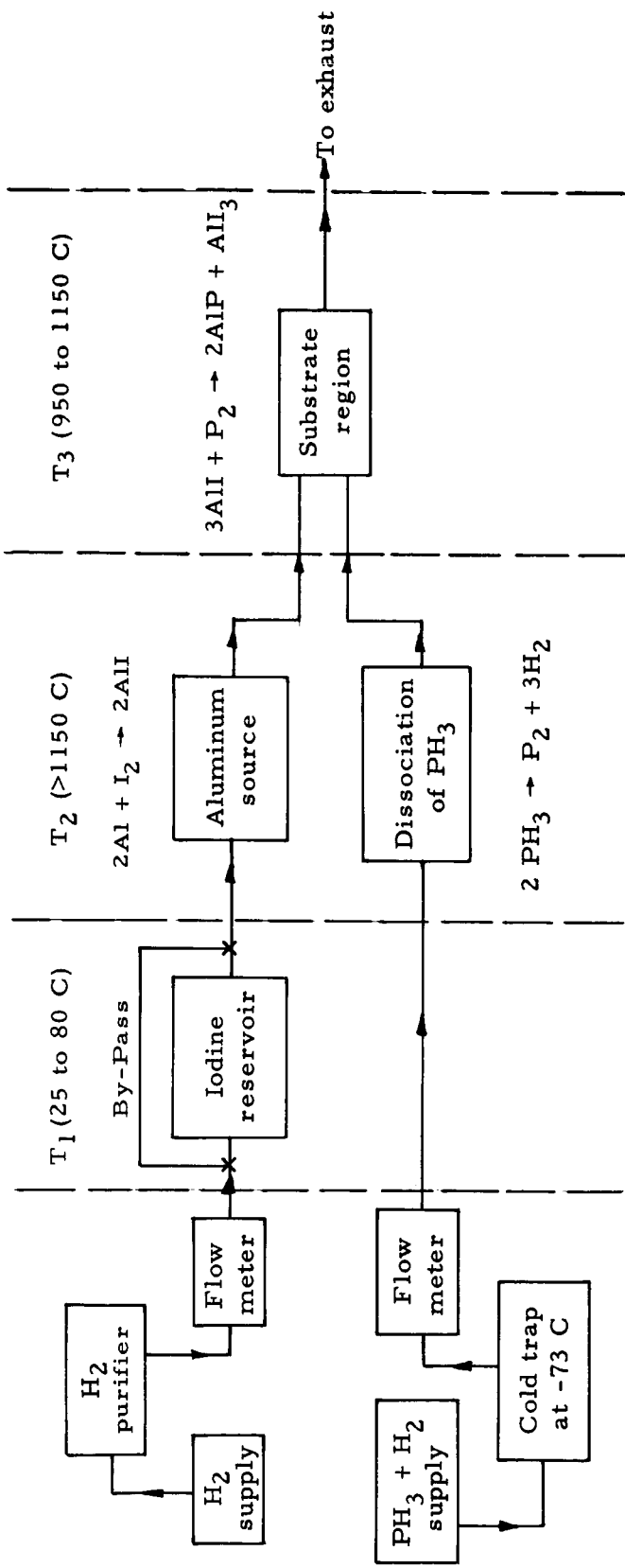
FIGURE 1. SCHEMATIC REPRESENTATION OF VAPOR FLOW SYSTEM FOR DEPOSITION OF AlP

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FIGURE 2. SCHEMATIC OF REACTOR SYSTEM

Scale ≈1:3

Labels in figure:
- Stainless steel end cap
- Exhaust
- Resistance furnaces
- Substrate on Alumina holder
- Alumina tubes
- Aluminum source
- $PH_3 + H_2$
- $I_2 + H_2$
- 39536

flow of hydrogen as a carrier gas at a flow rate of 500 to 1000 cm^3/min. The source of phosphorus currently being used is a mixture of PH_3 and H_2 and is brought into the system at a flow rate of 20 to 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 exits these vapors into the reaction tube proper at a point upstream of the substrate but downstream of the aluminum source. Some back diffusion of phosphorus against the predominantly left-to-right flow occurs at this point, depending on the difference between the flow rates of the hydrogen carrier gas directed through the iodine and PH_3-H_2 mixture. Phosphorus diffuses far enough upstream to reach the aluminum source if the iodine-stream flow becomes less than about 450 cm^3/min greater than that of the phosphorus stream.

Figure 3 shows in detail the design of a stainless steel end cap that is fitted on each end of the ceramic reactor system with vacuum-tight O-ring seals and provides entrance ports (ceramic tubes fitted with O-ring) and a stainless steel exhaust port (not shown) for waste disposal. During the preparation of AlP, these end caps are maintained at a temperature of 50 to 100 C.

Viton O-ring   Alumina tube

A-54310
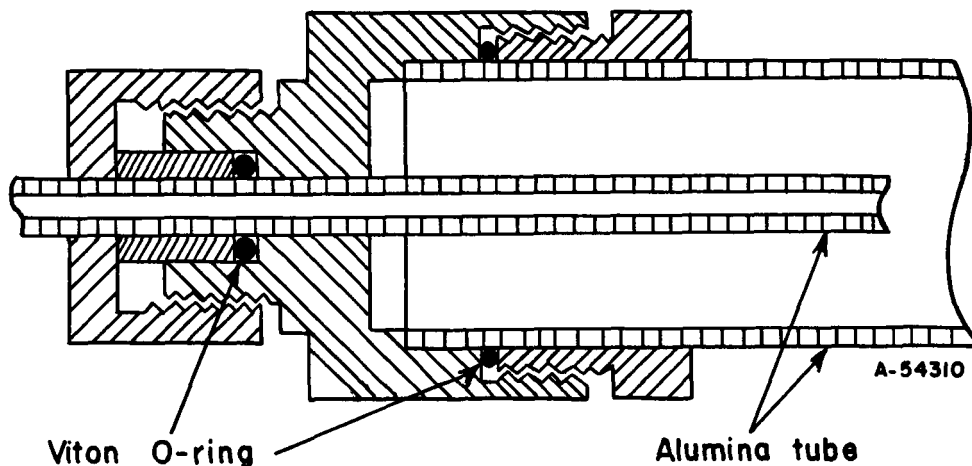
FIGURE 3.   SCHEMATIC OF STAINLESS STEEL END CAP

Full scale.

The ceramic system, as shown in Figure 2, has performed nicely with but one exception. After one or two experiments, the large-diameter ceramic tube usually will break. The break occurs at a position about 20 cm downstream from the left end of the furnace, where AlP first forms on the tube wall and where there is a steep temperature gradient. Since it is difficult to find tubes having the same diameter, the end caps

often have to be modified to fit each tube. The tube with the end caps can be retained for a larger number of experiments by using an alumina liner tube inside the reactor system and replacing the liner after one or two experiments.

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 aluminum is evaporated during this heat treatment.

The iodine used to transport the aluminum 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 4 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.

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*AIAG Metals, Inc., New York, New York.
**Gallard-Schlesinger Chemical Manufacturing Corporation, Garden City, New York.
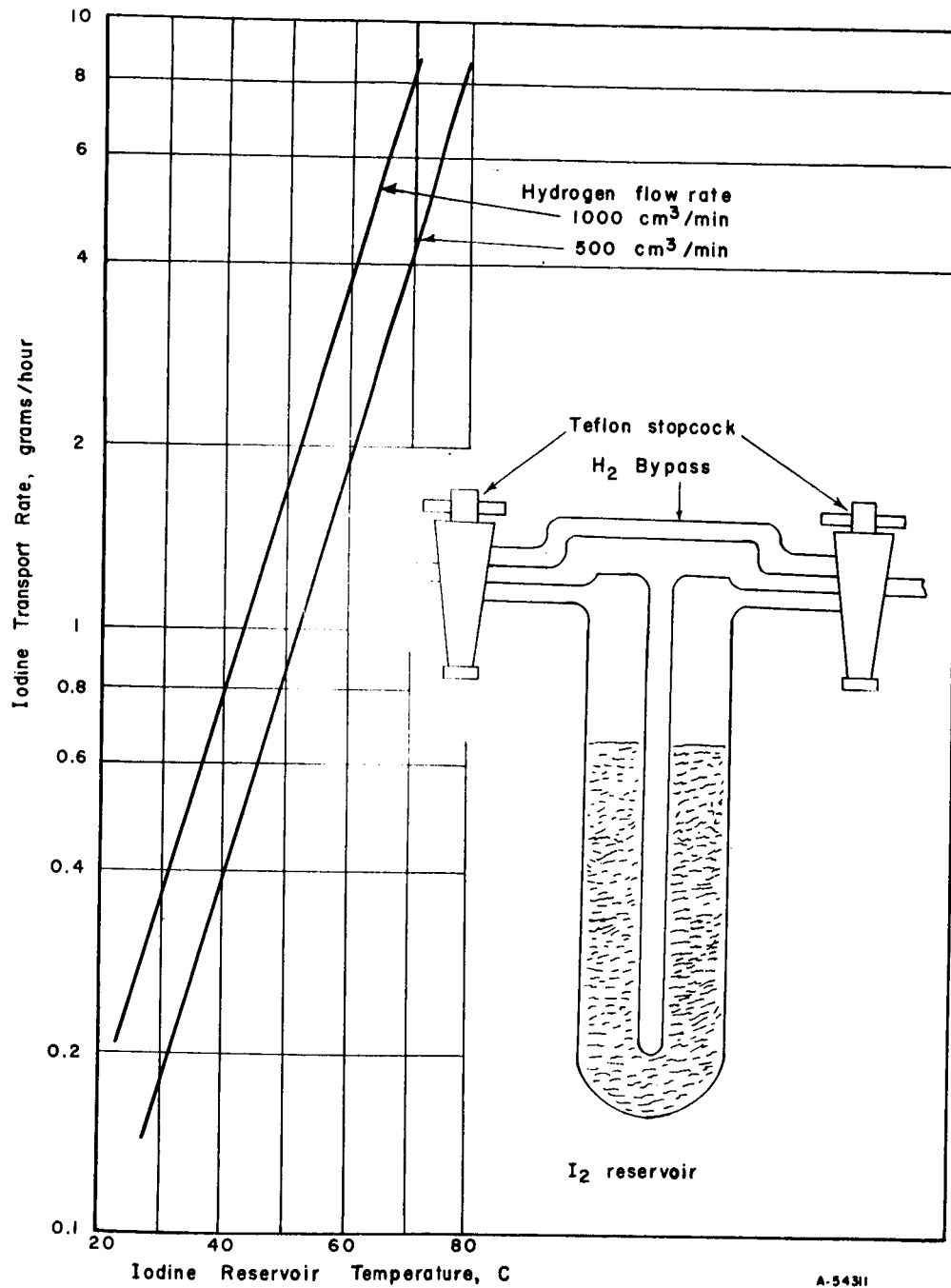***Matheson Company, Rutherford, New Jersey.

FIGURE 4.   IODINE TRANSPORT RATE AS A FUNCTION OF
            TEMPERATURE AND SCHEMATIC OF IODINE
            RESERVOIR

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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 is obtained only as cp grade and may be given several vacuum distillations prior to use. As in the case of the iodine, a large reservoir of PCl_3 is 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, 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.

The silicon substrates are single crystals which may have a variety of electrical characteristics. High-resistivity silicon has been used predominantly, because it can be polished to a finer finish than can heavily doped silicon. The silicon is given a final polish chemically by rotating it at 100 rpm in 9:1 HNO_3 : HF. After polishing, the substrate is boiled in a trichloroethylene bath for 2 minutes and the hot bath is then ultrasonically agitated for 2 minutes. Next the substrate is immersed in ultrasonically agitated methyl alcohol and rinsed thoroughly in filtered deionized water. The substrate is immersed in HF for 1 minute and rinsed throughly in alcohol prior to being loaded into the reactor system under a flow of dry argon or hydrogen gas.

Preparation Procedure and Chemistry

The following is a description of the procedure currently used for the vapor deposition of AlP onto silicon substrates. 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 of <10^{-3} torr at temperatures in excess of their ultimate use temperatures. 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. After a final

*The American Agricultural Chemical Company, New York, New York.

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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 4). 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.
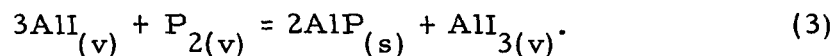
The vapor-deposition scheme was designed to take advantage of the formation of a subiodide of aluminum at the aluminum source, according to the reaction

$$Al_{(1)} + \frac{1}{2} I_{2(v)} = AlI_{(v)}, \tag{1}$$
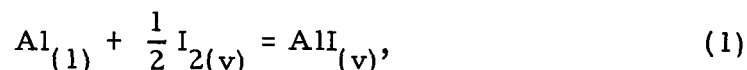
and the release of free aluminum from the AlI in the substrate region, according to the reaction

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

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 5 is a plot of the free energies of formation of several aluminum halides as a function of temperature (Ref. 11). 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 5 for comparison. Aluminum-source
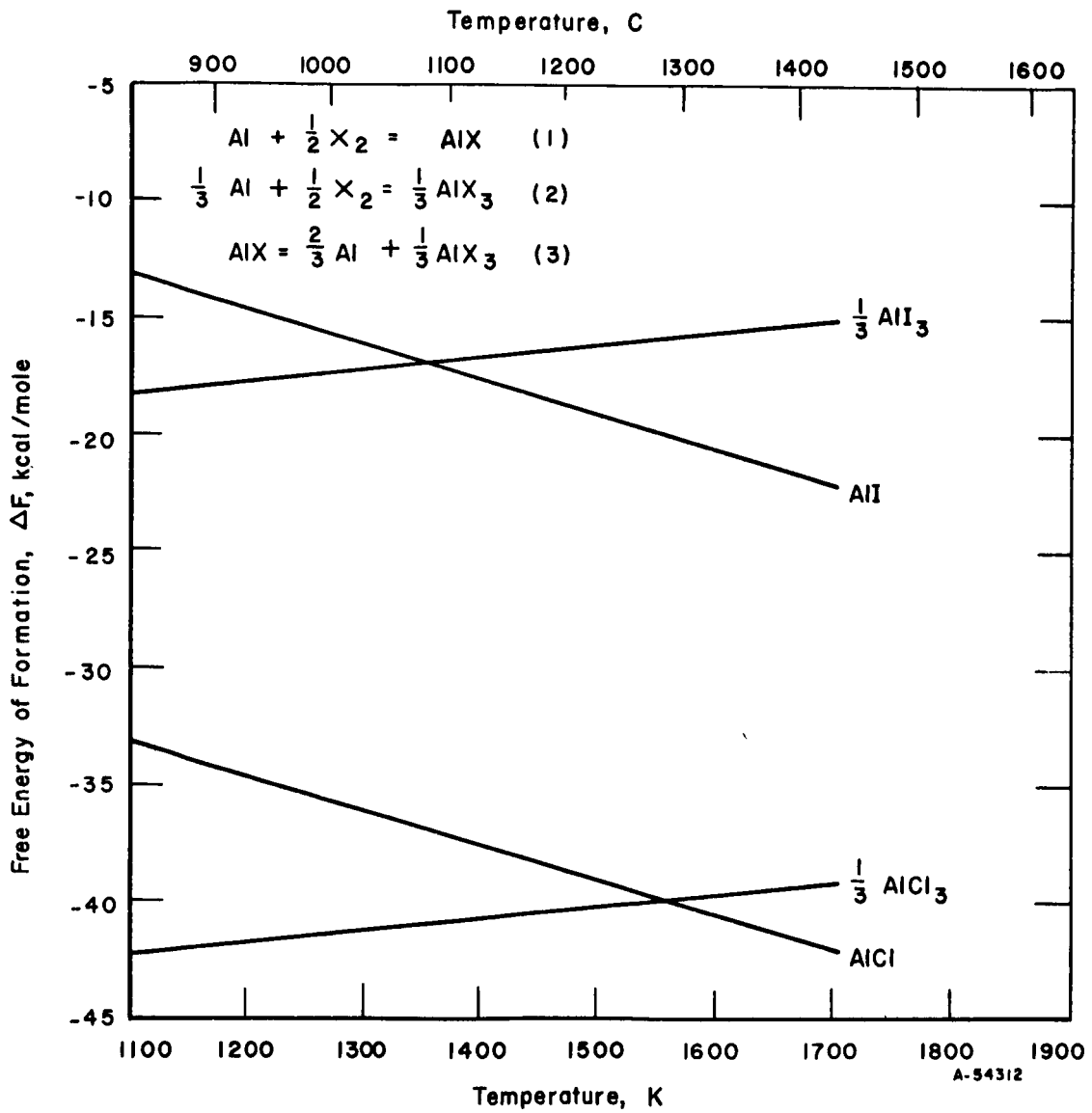
FIGURE 5.   FREE ENERGIES OF FORMATION OF ALUMINUM
            HALIDES AS FUNCTIONS OF TEMPERATURE

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temperatures in excess of about 1300 C would be required in order 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 6 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.

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.

Electrical Measurements

Samples for electrical-properties studies have been obtained from AlP layers grown on silicon substrates and from needles and crystals that were nucleated and grew on the P$_2$ inlet tube and other ceramic parts of the system. The silicon substrates were lapped away, leaving the AlP layers. Parallelepipeds were cleaved from the layers, and solder contacts were applied with ultrasonic agitation. To facilitate measurements to 500 C, pressure contacts were placed on thin layers of metal at points on the AlP. Well-formed needles of AlP were used without further shaping, and contacts were applied as discussed above. It is noted that a soldered contact is more easily made on an as-grown surface of AlP than on a lapped or polished surface.
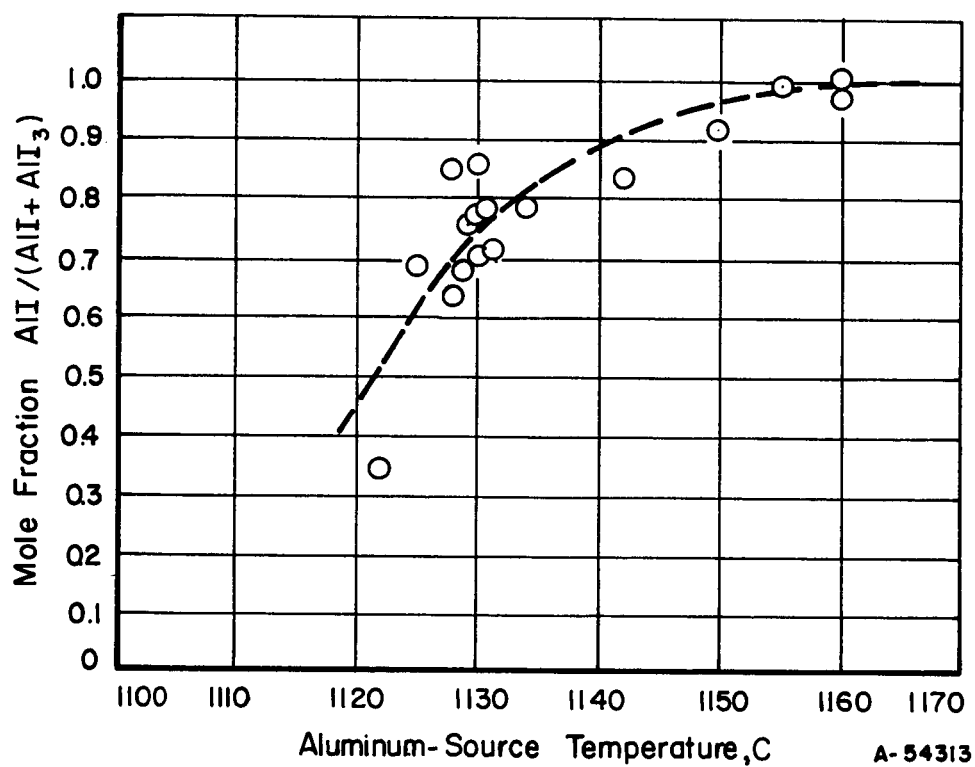
FIGURE 6.   MOLE FRACTION OF AlI PRODUCED BY REACTION OF
ALUMINUM AND IODINE AT VARIOUS ALUMINUM-
SOURCE TEMPERATURES

The electrical properties of prime interest as standards of material quality and device potential are electrical conductivity, Hall coefficient, carrier mobility, and carrier concentration. Of these, the first two, σ and R_H, are determined experimentally. Measurements of σ and R_H and their temperature dependence yield values of charge-carrier concentration, distinguish between conduction by electrons and conduction by holes, and yield values of carrier mobility.

EXPERIMENTAL RESULTS

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.

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. In addition to the large silicon contents in AlP samples prepared in a quartz reactor, copper concentrations in the AlP were relatively large, e.g., AlP from the quartz reactor (see Experiment Number 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.

It is to be noted that GaP and GaAs substrates were substituted for the silicon substrates 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 Sample 28 in Table I. It is noted, however, that these layers contained about 50 ppm silicon as

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TABLE I

SILICON CONCENTRATIONS IN SELECTED SAMPLES OF AlP

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.

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 which 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 Samples 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.

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 (Ref. 12) 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 grown 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. With the exception of the aforementioned correlation of electron concentration and silicon content and of resistivity and the presence of oxygen, the electrical properties of the AlP samples show no apparent dependence on preparation conditions or crystal morphology. 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 samples, 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. This material was grown at about 1150 C using a phosphorus-to-aluminum ratio of about 0.6. Sample 107 has a low carrier concentration (4.5×10^{17} cm^{-3}). However, 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.

Figure 7 is a plot of resistivity and Hall coefficient as functions of temperature for a relatively low-resistivity sample of AlP (Sample 95). Figure 8 is a plot of resistivity as a function of temperature for two samples of relatively high resistivity, obtained in preparations where the cold trap was not present in the PH$_3$ vapor train.

Character of Deposits

In general, the experimental preparations yielding the most promising crystal-growth results have been made 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 on {111} and {100} silicon substrates was shown to be epitaxial, as determined from the analysis of back-reflection X-ray Laue patterns. These layers have been 50 to 500 μm thick and some were removed from the substrates prior to the X-ray analysis.

Layers of AlP prepared using lower substrate temperatures (950 to 1050 C) and no temperature gradient in the substrate region have been polycrystalline. In the past (Ref. 3), 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 establishment of a temperature gradient across the substrate may have

TABLE II
ELECTRICAL PROPERTIES OF AlP SAMPLES

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	298	0.0654	75	1.3×10^{18}
	77	0.304	30	6.8×10^{17}
97	298	0.0555	80	1.4×10^{18}
	77	0.455	31	4.5×10^{17}
107	298	2.68	5	4.5×10^{17}
110A	298	0.0246	41	6.2×10^{18}
110B	298	0.0416	33	4.5×10^{18}
113	298	0.0661	23	4.1×10^{18}
118	298	0.0704	50	1.8×10^{18}
104[a]	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.
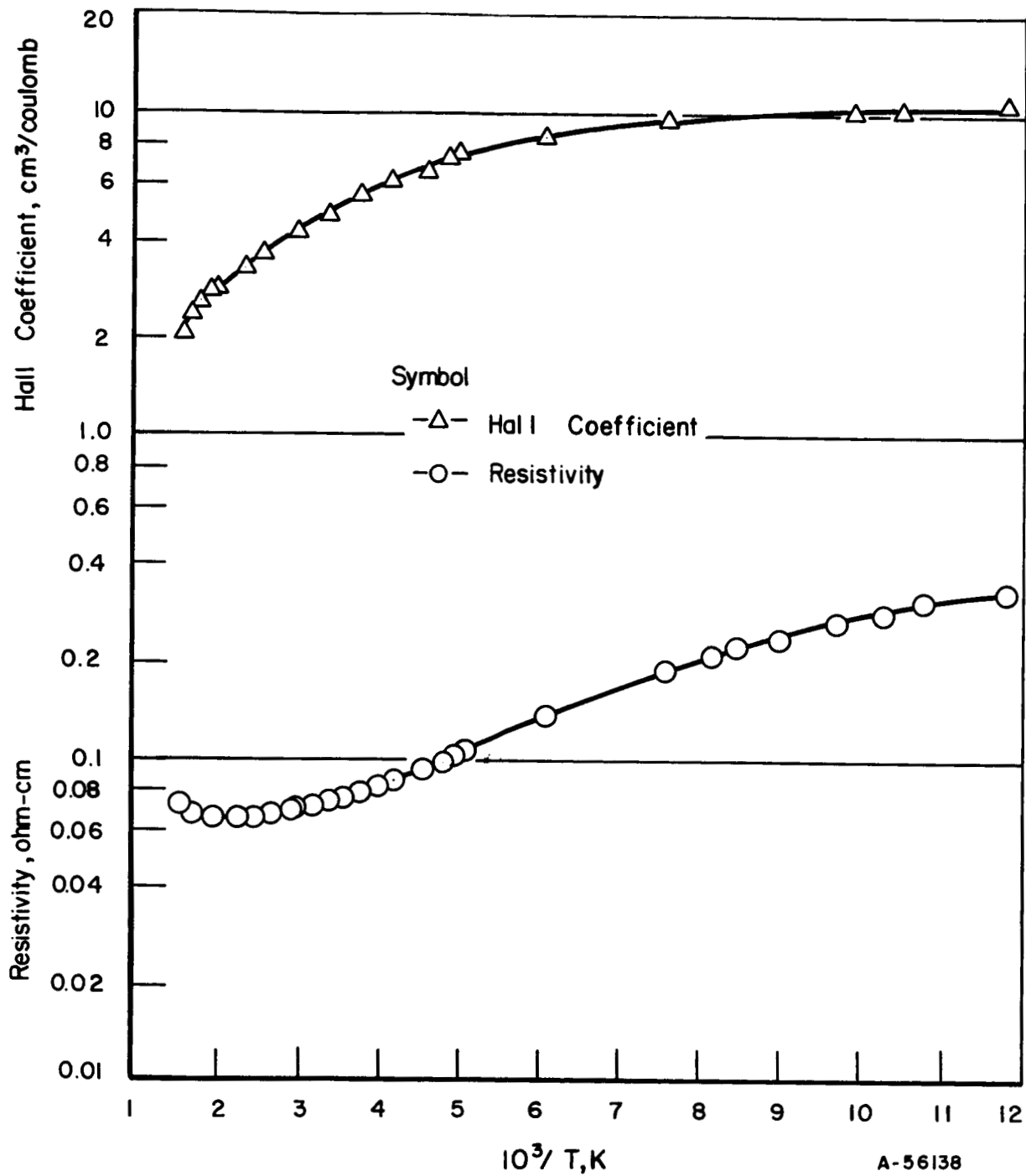
18

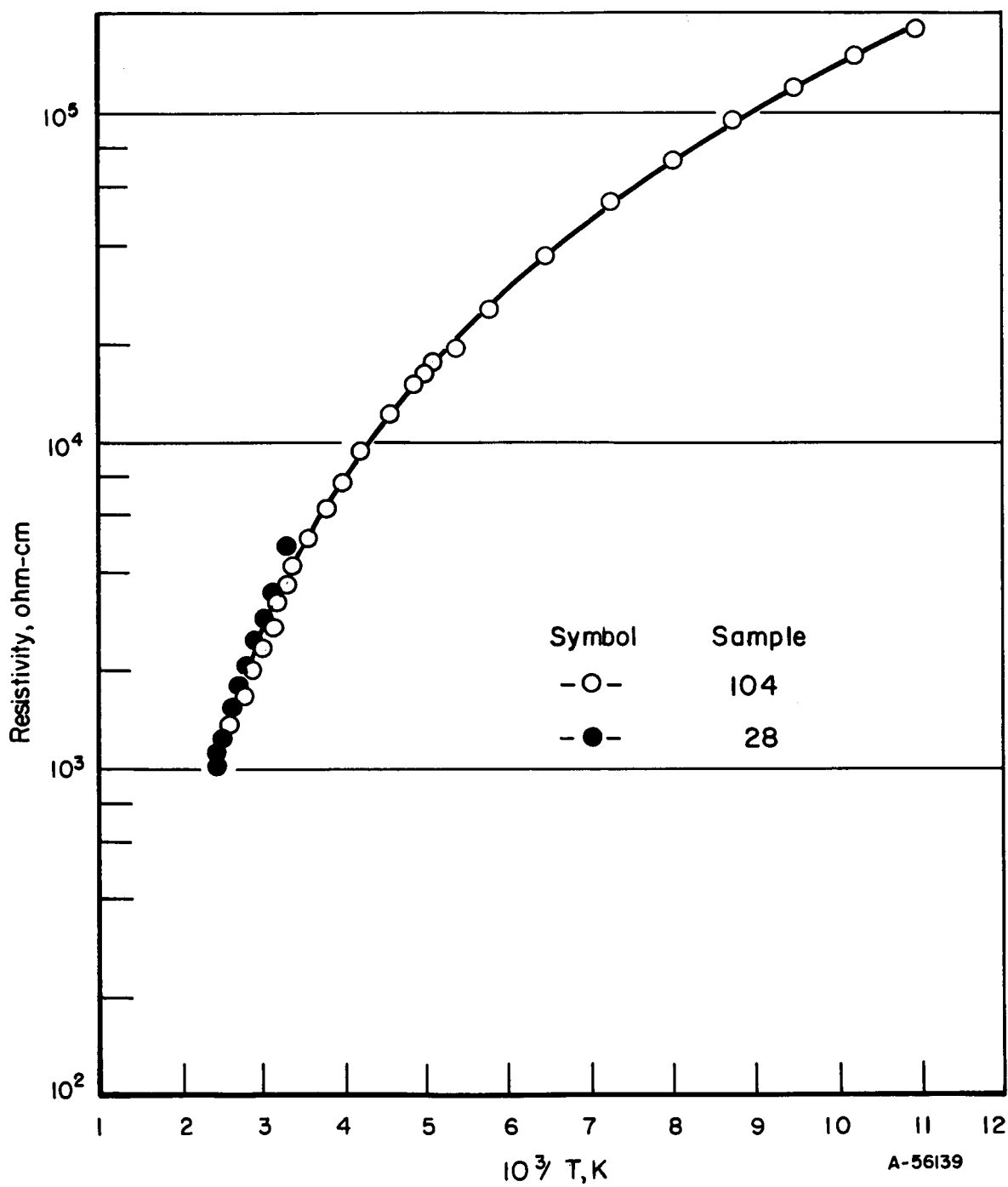FIGURE 7. HALL COEFFICIENT AND RESISTIVITY OF
n-TYPE AlP SAMPLE 95

19

FIGURE 8.   RESISTIVITY OF OXYGEN-DOPED AlP

20

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.

As indicated, 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 to assume 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 in color. 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 in color. 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 in color and exceedingly transparent as grown.

Crystals of AlP are chemically stable in dry air but 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, 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 growth scheme. Such crystals were still intact and usable after an exposure of 24 hours to ambient air at approximately 50 percent 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.

ANALYSIS OF RESULTS AND RECOMMENDATIONS

The results to date have shown an improvement in the quality of AlP layers deposited by vapor-growth techniques. Reductions in impurity content by eliminating the use of quartz parts in the high-temperature regions of the reactor are encouraging. However, the electrical properties and spectrographic analysis of the product formed in the ceramic reactor system suggest that additional purification is required. It is most important that this purification be accomplished, since investigations in other areas are dependent on the availability of high-quality crystals. At the moment, the major impurity problem is silicon and large concentrations are found in the AlP even when the all-ceramic reactor system is used. The use of GaAs and GaP substrates in place of silicon substrates eliminated the silicon substrate as a major source of silicon impurities at the concentrations in question. Upgrading of the purity of the ceramic parts used in the reactor system is proceeding as "trade offs" become available. Additional care may well be needed in cleaning and outgassing procedures.

Although the AlP produced in the ceramic system still requires further purification, this material is far superior to that produced in a quartz system. It appears that by including some oxygen in the preparation scheme, an additional lowering of the free-carrier concentration in the AlP can be achieved by the elimination of silicon electrically if not physically. Hence, a number of additional investigations are now possible, including optical transmission and photoconductivity studies, formation of p-n junctions by the addition of a reasonable concentration of dopants, and electrical contact studies on a nondegenerate material.

The presence of the stainless steel cap on the upstream end of the reactor system and the accompanying difficulties that go with trying to make the connections airtight may be a source of impurities. Investigations are under way at the present time on the possibility of increasing the aluminum-source temperature to the point where the phosphorus can be passed over this source without halting the production of AlI. Success along these lines would permit the use of a single inlet port on the upstream end, which could be fashioned out of ceramics. This would also permit the use of lower flow rates of the vapors, which is likely to contribute to better crystal growth.

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