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VAPOR-PHASE GROWTH TECHNIQUE AND SYSTEM FOR SEVERAL III-V COMPOUND SEMICONDUCTORS

BY

J. J. TIETJEN, R. CLOUGH, R. ENSTROM, M. ETTENBERG,
H. P. MARUSKA, AND A. G. SIGAI

INTERIM SCIENTIFIC REPORT NO. 3

APRIL 1970

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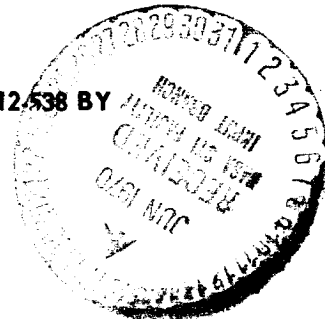
ELECTRONICS RESEARCH CENTER
CAMBRIDGE, MASSACHUSETTS
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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RCA Laboratories
Princeton, New Jersey

SUMMARY

During this nine month contract period, excellent results have been realized for the vapor-phase growth of III-V compounds containing aluminum. Single-crystalline AlAs has been prepared with unprecedented stability and good electrical properties, including reproducible electron mobilities in excess of 280 cm^2/V-sec, which is the highest value ever reported for AlAs. In addition, electron carrier concentrations as low as 10^{16}/cm^3 have been achieved with this material, and it has been used to fabricate the first stable AlAs p-n junction structures. The requisite conditions have been defined for the growth of AlP and AlN, and a technique has been developed for the preparation of AlSb.

Improvements have been made for the growth of GaN, and this has resulted in improved crystallinity, surface perfection, and electrical properties for this compound. Also, improved control of the composition of $Ga_{1-x}In_xP$ has been obtained, and higher electron mobilities have been achieved with GaSb layers.

As a result of these advances, and those realized during the first two years of this contract, virtually all of the objectives of developing a compatible vapor-phase growth system for the preparation of several III-V compounds have been attained. The system developed, to date, has the capability of preparing an outstanding number of materials as single-crystalline layers, doped either n- or p-type, and in the form of multilayer structures, including p-n junctions. Included in these materials are GaAs, GaP, GaSb, GaN, InAs, InP, AlAs, AlP, AlN, $GaAs_{1-x}P_x$, $GaAs_{1-x}Sb_x$, $Ga_{1-x}In_xAs$, $Ga_{1-x}In_xP$, $InAs_{1-x}P_x$, and $Ga_{1-x}Al_xAs$. Further, these materials have found application in a large number of devices, many of which exhibit exceptional characteristics. These include varactor diodes, transferred electron oscillators, electroluminescent diodes, injection lasers, high-temperature rectifiers and transistors, electro-optic modulators, secondary-emission dynodes, and photocathodes.

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I. INTRODUCTION

During the first year of this contract, the primary objective was to develop a compatible vapor-phase growth system for the preparation of GaAs, GaP, GaSb, InAs, InP, InSb, and selected alloys of these compounds. Further, the system was to have the capability of providing both n- and p-type doping and the preparation of multilayer structures. To accomplish these objectives, the RCA method of vapor growth, used previously with great success for the preparation of GaAs and $GaAs_{1-x}P_x$ alloys, was further developed to permit the preparation of compounds containing In and Sb.

In this way, all of the above compounds, except InSb, were prepared as single crystals. In addition, alloys of $GaAs_{1-x}P_x$, $InAs_{1-x}P_x$, $GaAs_{1-x}Sb_x$, $Ga_{1-x}In_xAs$, and $In_{1-x}Ga_xP$ were also grown as pure, single-crystalline epitaxial layers. Also, p- and n-type doping and the preparation of multi-layer structures in selected materials were achieved, which demonstrated the ability of this vapor-phase system to fulfill the objectives of the program.

In order to extend the utility of this vapor-growth system, work during the second year focused on the preparation of III-V compounds containing Al and nitrogen by the addition of Al and NH_3 sources. Also, the antimonide work was completed, and the growth and characterization of $In_{1-x}Ga_xP$ alloys was continued because of its potential for visible electroluminescence. Again the system demonstrated its ability to meet the program objectives, even though several of these goals were exceptionally difficult to attain because of problems related to the instability of SbH_3 at room temperature and the corrosiveness of the aluminum chlorides.

The work during this past nine-month period has emphasized the preparation of those materials which showed promise during previous periods, and without exception, significant improvements in material quality have been made. This includes the growth of AlAs, GaN, GaSb, and $In_{1-x}Ga_xP$ alloys. In addition, the vapor growth of AlN, AlP, and $In_{1-x}Ga_xN$ was investigated. The growth of such a wide variety of III-V compounds further demonstrates the versatility and utility of this vapor-growth system.

II. TECHNICAL DISCUSSION

A. Growth of GaN

Significant progress has been made in the vapor growth of GaN, and these crystals are the first reported samples of GaN suitable for good electrical and optical evaluation of this compound. It has been determined that GaN has a *direct* energy bandgap of 3.39 eV, and that undoped crystals prepared by this method have a very high, inherent electron concentration, typically above $10^{19}/cm^3$, which is probably related to a high density of nitrogen vacancies. Conducting *p-type* specimens have been prepared using Ge as the dopant; but this

result has been difficult to reproduce, and the samples have been electrically inhomogeneous. A detailed description of this work is given in Appendix A.

The most important remaining problem related to the preparation of this compound is that of achieving reproducible p-type conductivity. To accomplish this it appears necessary to reduce the high-inherent donor concentration, and, therefore, several approaches have been investigated for reducing the net donor concentration by suppressing the nitrogen-vacancy concentration. Two samples were annealed in an autoclave under ammonia pressures of 3 and 7 atmospheres at 800° and 900°C, respectively, for 18 hours. However, in each case the specimen decomposed, probably because excessive ammonia decomposition occurs at these temperatures. The decomposition products of ammonia, molecular nitrogen, and hydrogen are not effective in preventing GaN decomposition. In another set of experiments, GaN was grown at temperatures as low as 775°C instead of the usual 850°C. However, the net donor concentration was not reduced in these growths and was sometimes slightly higher than the usual values. In addition, attempts to dope these layers with Ge did not produce homogeneous p-type material. In a third experiment, the ammonia was introduced into the reaction tube in close proximity to the deposition zone to prevent premature decomposition of the ammonia. Although this change doubled the growth rates and resulted in higher mobility values (150 cm^2/V-sec), it did not effect lower donor concentrations.

Additional attempts to reduce the net donor concentration by reducing the nitrogen-vacancy concentration were made by annealing a vapor-grown GaN sample in a nitrogen-atmosphere glow discharge. It had been shown previously that during a glow discharge the gas being used becomes incorporated in the cathode material; i.e., in a glow discharge of nitrogen with a molybdenum cathode, the nitrogen ionized and diffused into the molybdenum in substantial amounts. It was felt that if a GaN cathode were used in conjunction with a nitrogen glow discharge, atomic nitrogen could be incorporated into the GaN lattice to annihilate the nitrogen vacancies formed during vapor growth. Therefore, nitrogen pressures ranging from 2 to 10 mm, voltages up to 1500 V, and GaN temperatures up to 800°C were investigated, but no appreciable, reproducible change in carrier concentration could be effected.

Alternatively, it is possible that the high donor concentrations in the GaN may be related to strain-induced defects in the epitaxial layer resulting from lattice parameter or thermal expansion mismatch between the epitaxial layer and the substrate. For example, the thermal expansion coefficient along the "a" direction is 9.4 x 10^{-6} cm/cm°C for the sapphire and is 5.6 x 10^{-6} cm/cm°C for GaN, and electron-microscopic analyses of GaN layers on sapphire have shown large numbers of dislocations to be present. To eliminate these sources of mismatch and thus the associated defects, it is desirable to have GaN substrates. Therefore, two potential sources of GaN substrate material were investigated. In one case, the growth of GaN platelets from a solution of GaN in Sn was attempted, but only GaN powder was produced. In another case, the growth of a very-thick GaN layer on a sapphire substrate was investigated so that the sapphire might be subsequently polished away leaving

a homogeneous single-crystalline GaN layer for use as a substrate. Such a sample was grown for 5 1/2 hours to produce a layer 30-mils thick, and then slowly cooled to prevent cracking. However, the sample was very badly bowed, which prevented polishing off of the sapphire substrate. Next, a thin (2-mils thick instead of 10-mils thick) sapphire substrate was used for the growth of another 30-mils thick GaN layer, and bowing of the GaN was eliminated. This layer is now being processed for future use as a substrate in a homoepitaxial growth of GaN.

Additional attempts to achieve p-type conductivity involved trying to incorporate higher concentrations of Ge in the GaN layers. Since more Ge might be incorporated at temperatures higher than the normal growth temperature of 825°C, a study was undertaken to determine the conditions for growing GaN at higher temperatures. As a result, it is now possible to grow GaN, on sapphire substrates, at temperatures as high as 970°C without degrading its electrical properties. In fact, at this elevated temperature, the crystallinity of the deposits is enhanced and improved surface quality results. Also, a slight reduction in the net electron concentration was obtained; but despite these improvements, Ge-doped specimens have not yet yielded uniform p-type conductivity.

B. Growth of $In_{1-x}Ga_xN$

$In_{1-x}Ga_xN$ alloys have never been prepared before, and it is possible that such alloys with a bandgap smaller than GaN can be more easily doped with acceptor impurities than can pure GaN. For the growth of the $In_{1-x}Ga_xN$ alloys, the GaN vapor-growth system has been modified to permit the use of separate Ga and In sources, and proper operation of this system was demonstrated by the preparation of GaN. In a series of five runs, the growth of $In_{1-x}Ga_xN$ alloy layers on sapphire substrates was attempted using deposition temperatures ranging from 765° to 835°C and metal-source temperatures ranging from 875° to 940°C. However, to date only GaN was found to be present in the vapor-grown layers probably because the experimental conditions used favored growth of this compound since InN is unstable above 600°C.

C. Growth of AlAs, AlN, and AlP

The large, indirect bandgap (> 2.1 eV) of AlAs makes it an especially desirable material for high-temperature device applications or optical applications in the visible region of the spectrum. The high melting point of this compound and the high reactivity of aluminum create initial problems in high-purity preparation. Additional limitations have been the instability of AlAs in air and its low electron mobility. Reports of complete degradation of grown layers in 10 minutes (Ref. 1) would seemingly indicate a limited usefulness, and the highest reported room-temperature electron mobility is 180 cm^2/V-sec (Refs. 2,3).

The basic vapor-growth technique (Ref. 4) has been modified to accommodate the growth of Al-containing compounds and has been used in this study for the preparation of AlAs. This has resulted in n-type AlAs having excellent stability and high electron mobilities.

The growth system employs the standard quartz tube (Ref. 4) with accommodation for a high-purity (99.7%) alumina liner in the region of the tube containing the aluminum. The aluminum (99.999%) starting material is contained in high-purity (99.7%) alumina boats. It is not necessary to protect the growth system in the deposition region, since the initial AlAs deposit in that region seems to afford adequate resistance to attack of the quartz by Al or $AlCl_x$.

Aluminum is transported as the chloride by passing Pd diffused H_2 carrier gas containing 0.2% HCl by volume over the liquid aluminum at 1050°C. The aluminum chloride is then mixed with arsine and the AlAs is formed and deposited on GaAs substrates at 1000°C. Before mixing with the $AlCl_x$ the AsH_3 is 2% by volume in the H_2 carrier gas.

It has been found necessary to have a large liquid-aluminum surface since some surface reaction area can be eliminated through the formation of some Al_2O_3 on the aluminum liquid. Therefore, three to five aluminum boats are employed in series with the first one or two acting as getters for the small amounts of impurities, principally oxygen or water vapor in the HCl-H_2 mixture, and to promote complete reaction of HCl with the Al. Reaction of $AlCl_x$ and AsH_3 or their decomposition products seems to take place at the position of initial mixing independent of reactant concentration or temperature, indicating a large driving force for the reaction. In order to deposit AlAs on the substrate, growth must take place under conditions of relatively high gas velocity; hence, the alumina liner is capped by a high-purity boron nitride plug with small holes which creates a relatively high $AlCl_x$ gas velocity at the substrate.

Under standard conditions the growth rate can be varied between 10 and 100 μm/hr depending on reactant concentrations. In most cases grown layers are either epitaxial single crystals or highly oriented large-grained poly-crystals.

The carrier concentrations of the AlAs layers measured on unsupported AlAs to supplement earlier measurements on semi-insulating GaAs (> 10^5 Ω-cm) substrates ranged from 10^{16} to 5×10^{18}/cm^3 for samples grown under slightly varying conditions. For samples with carrier concentrations $\sim 10^{17}$/cm^3, room-temperature electron Hall mobilities as high as 280 cm^2/V-sec were achieved and these represent the highest mobilities reported to date for AlAs. Carrier concentrations of 5×10^{18}/cm^3 had associated room-temperature mobilities of about 100 cm^2/V-sec.

Ohmic contacts were made to the AlAs layers by a combination of ultrasonic soldering of indium followed by an anneal in hydrogen for 5 minutes at 800°C.

Small single crystals of AlAs 4-mils thick were removed from the substrate, and the optical absorption was measured as a function of wave-length. The optical density was plotted as a function of $(h\nu-E_g)^2$ for the indirect bandgap and fitted to a straight line giving a value for E_g of 2.20 ± 0.10 eV. Polycrystalline deposits of AlAs on sapphire provided the same optical results.

As previously mentioned, the stability of these layers is much improved over previously published results. Although samples are usually maintained in a vacuum desiccator, no visible deterioration of the material occurs for samples maintained in air for periods of up to a week. Diffused p-n junctions have been fabricated from this material and have maintained their original I-V characteristics for at least a month in normal room ambient conditions.

The lattice parameter of AlAs has been accurately measured as a function of temperature. The lattice parameter at 16°C is 5.6611 ± 0.0006 Å compared to GaAs, 5.653 Å; thus there is less than a 0.2% mismatch at room temperature. The lattice parameter of GaAs at 800°C is 5.683 Å compared to 5.6848 ± 0.0011 Å for AlAs at 812°C; thus at the normal-growth temperatures there is excellent lattice match. The initial calculation of the coefficient of thermal expansion for AlAs is $(5.15 \pm 0.2) \times 10^{-6}/°C$.

This system has also been employed for the growth of AlN and AlP by substituting NH_3 and PH_3, respectively, for the AsH_3. This has resulted in single-crystalline growth of both of these compounds.

To gain further insight into the growth of AlAs, the thermochemistry of the vapor growth of AlAs has been examined using the most recent data available (Refs. 5 through 10). In some respects the growth of AlAs and GaAs are analogous, in that HCl is used to transport the metal species, and AsH_3 is the source of As vapor. But, in other respects the growth is different because both the source and the deposition temperatures are about 250°C higher for AlAs than for GaAs. Also most growth of AlAs occurs at the point where the metal chlorides mix with the As vapor whereas GaAs deposits about 4 to 6 in. downstream from this point. A detailed comparison of the thermodynamics of the two compounds and the suggested chemical reactions occurring during vapor growth are given in Appendix B. These results, however, are based on assumed species and reactions between them. It is expected that an RCA-supported, high-temperature, mass-spectrometry study that is currently in progress will clarify the chemistry of the vapor-growth process. Nonetheless, it appears that certain conclusions can be made based on thermodynamic data. The monochlorides of Ga and Al are the principal species that react with arsenic vapor to form GaAs and AlAs respectively. Thus, even though $AlCl_3$ may be a large constituent of the reaction product of

Al with HCl, it does not lead to vapor deposition of AlAs. A similar situation probably also exists for AlSb and AlP, but it should be possible for $AlCl_3$ to react with NH_3 to form AlN, because of its larger free energy of formation.

D. Growth of $In_{1-x}Ga_xP$ Alloys

Work has continued on the growth of $In_{1-x}Ga_xP$ alloys because of the potential of this material for electroluminescent devices operating in the visible region of the spectrum. The major problems associated with the preparation of this material have been obtaining good control of the composition and avoiding high-defect concentrations in the epitaxial layers. Accordingly, a systematic study of the various growth parameters was undertaken in an effort to overcome these difficulties.

The effect on the alloy composition of the phosphine flow rate and the temperatures of the metallic sources, the center zone, and the deposition zone were individually examined, and the results are presented in Tables II through VII. For reference, the standard conditions used for the growth of an alloy containing about 80% GaP are given in Table I.

Table I

STANDARD CONDITIONS FOR GROWTH OF $IN_{.2}Ga_{.8}P$ ALLOY LAYERS

Furnace	Temperature, °C	Gas	Flow Rate ml/min
Gallium Zone	850	HCl over indium	4.0
Indium Zone	980	Hydrogen carrier gas	300
Center Zone	1000	HCl over gallium	0.4
Growth Zone	775	Hydrogen carrier gas	30
		Phosphine (100%)	60
		Hydrogen carrier gas	540

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Table II

EFFECT OF GALLIUM-ZONE TEMPERATURE ON $In_{1-x}Ga_xP$ COMPOSITION*

Gallium Temperature (°C)	Composition (% GaP)
900	82.9
850	79.3
770	78.8
650	77.7

*Prepared with other growth conditions as in Table I.

Table III

EFFECT OF INDIUM-ZONE TEMPERATURE ON $In_{1-x}Ga_xP$ COMPOSITION*

Indium Temperature (°C)	Composition (% GaP)
1100	82.6
950	86.5-94.1
800	90.0

*Prepared with other growth conditions as in Table I.

Table IV

EFFECT OF CENTER-ZONE TEMPERATURE ON

$In_{1-x}Ga_xP$ COMPOSITION*

Temp. of Center Zone, °C	Composition (% GaP)
1100	23.8
1000	27.9
900	21.4

* Prepared with other growth conditions as in Table I, but using a constant, lower HCl_{Ga}/HCl_{In} ratio.

Table V

EFFECT OF GROWTH TEMPERATURE ON

$In_{1-x}Ga_xP$ COMPOSITION*

Temp. of Center Zone, °C	Composition (% GaP)
875	73.0
775	51.7
675	44.4
575	22.0

* Prepared with other growth conditions as in Table I, but using a constant, lower HCl_{Ga}/HCl_{In} ratio.

Table VI

EFFECT OF PHOSPHINE FLOW RATE ON COMPOSITION OF

$In_{1-x}Ga_xP$ ALLOYS RICH IN GaP*

Flow Rate of Pure PH_3 (ml/min)	Composition (% GaP)
22	81.0
60	83.3
290	83.3

* Prepared with other growth conditions as in Table I.

Table VII

EFFECT OF PHOSPHINE FLOW RATE ON THE COMPOSITION OF

$In_{1-x}Ga_xP$ ALLOYS RICH IN InP*

Flow Rate of Pure PH_3 (ml/min)	Composition (% GaP)
22	34.1
60	29.3
290	33.3

* Prepared with other growth conditions as in Table I, but using a constant, lower HCl_{Ga}/HCl_{In} ratio.

It may be seen that except for the growth temperature, the composition is virtually independent of the other parameters. The dependence on the growth temperature may be due to the higher dissociation pressure of the InP-rich compounds, so that more InP is incorporated in the alloys at lower deposition temperatures, or to the temperature dependence of the growth reactions.

In addition to the growth temperature, the composition may be controlled by adjusting the ratio of the HCl flow over the gallium with respect to that over the indium as shown in Figure 1. Only a small flow of HCl to the Ga is needed for most alloys, and to adjust this ratio most effectively, a prediluted mixture of 3 to 10% HCl in H_2 is used. Below this concentration range, the mixture is unstable since HCl is absorbed preferentially on the walls of the gas cylinder. The results shown in Figure 1 are preliminary, and additional work will have to be done to establish more carefully the exact relationship between the composition and the HCl-flow ratio.
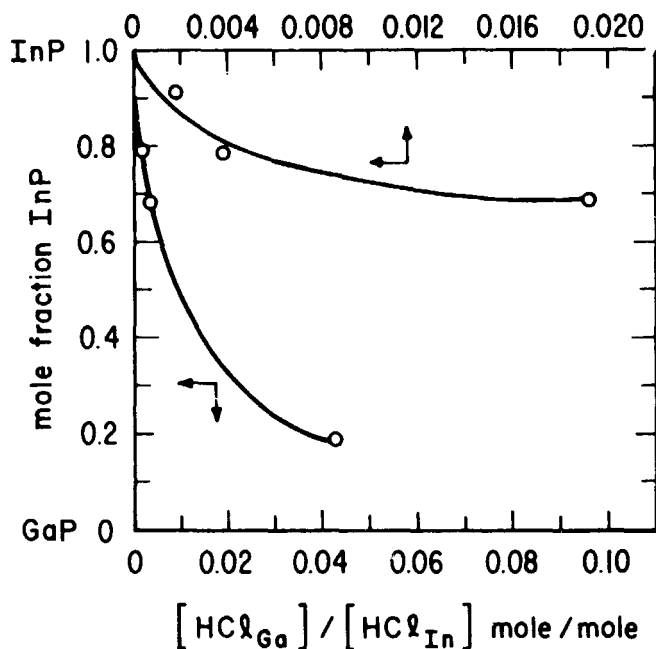

Figure 1. Composition of $In_{1-x}Ga_xP$ alloy layers as a function of HCl flow ratio to the Ga and In sources.

We had found previously that rapid diffusion of Zn from the p-type $In_{1-x}Ga_xP$ alloy layer through the alloy n-type layer, and then into the GaAs substrate produced electroluminescent diodes emitting infrared rather than visible light. This problem has now been completely eliminated by reducing the dopant concentrations to p $\sim$ 5 x 10^{18} cm^{-3} and n $\sim$ 5 x 10^{17} cm^{-3}. Using these doping concentrations, $In_{1-x}Ga_xP$ alloy p-n junction structures were prepared on n-type GaAs substrates, and emission at 7300 Å and 5700 Å

was observed for structures containing 40 and 88% GaP, respectively. In addition, for the latter alloy, uniform emission over the entire surface of the diode was achieved for the first time.

The diode efficiencies typically have been low, i.e., about 10^{-6} at 300°K and 10^{-4} at 77°K, and these low quantum efficiencies may be related to metallurgical imperfections. In fact, the rapid diffusion of Zn observed at high Zn concentrations in undoubtedly related to a high density of defects, particularly dislocations. Indeed, transmission electron-microscopic examination of several alloy layers has shown a high density of dislocations ($> 10^7$ cm^{-2}) and a well-developed subgrain structure. This high dislocation density could result from either lattice mismatch, thermal-expansion mismatch, or both. While it would be possible to minimize the lattice-constant mismatch by growing alloys having compositions near In$_{.43}$Ga$_{.57}$P on GaAs, the thermal-expansion mismatch would still be fairly large. The best procedure would be to grow these alloys on either InP or GaP and then grade the composition of the material from that of the substrate to the final alloy composition. Initially, large-grained (2 to 4 mm grain size) polycrystalline InP and GaP substrates have been used, and In$_{1-x}$Ga$_x$P alloy layers were prepared by grading from the respective terminal compound composition to the final alloy composition. However, only samples with poor surfaces resulted. Therefore, single-crystalline InP and GaP substrates, which only recently have become available, have been ordered so that a better evaluation can be made of the effect of the substrate on the crystalline perfection of the vapor-grown layer.

Mass spectrometric analyses were made of two electroluminescent diode structures to determine if a basic difference in impurity concentration exists between diodes of widely different efficiencies. However, the data obtained did not provide any conclusive answers to this question. Both diodes exhibited low purity.

E.   Growth of GaSb

GaSb and GaAs$_{1-x}$Sb$_x$ alloys can be vapor grown using stibine (SbH$_3$) as the source of antimony, but the use of this gas presents more storage and handling problems than do arsine or phosphine because stibine is quite unstable at room temperature. In the present study, we have used elemental antimony transported with HCl as a source for the preparation of single-crystalline layers of GaSb and GaAs$_{1-x}$Sb$_x$ alloys on GaAs substrates.

The samples are grown in the same dual-source growth tube that has been used for the preparation of In$_{1-x}$Ga$_x$P alloys. The standard conditions for the growth of GaSb by this technique are given in Table VIII.

Antimony transports quite readily with HCl, so that a low temperature (below its melting point) and highly diluted HCl concentrations are used. Measurements of weight loss of the antimony boat indicate that the antimony is transported primarily as the monochloride (SbCl).

Ordinarily, the growth rate is very low (< 5 μm/hour) which prohibits removal of the layers from the substrate, so that layers are usually grown

Table VIII

STANDARD CONDITIONS FOR GROWTH OF GaSb ON A GaAs SUBSTRATE

USING ELEMENTAL GALLIUM AND ANTIMONY

Furnace	Temp., °C	Gas	Flow Rate ml/min
Antimony Zone	575	100% HCl over antimony	0.24
Gallium Zone	950	Hydrogen carrier gas	2600
Center Zone	1000	100% HCl over gallium	4.0
Growth Zone	650	Hydrogen carrier gas	1400

on semi-insulating GaAs, in order that electrical measurements can be made. For one sample, a mobility of 420 cm^2/V-sec and a net hole concentration of 1.2×10^{17} cm^{-3} was obtained which is substantially higher than the highest hole mobility of 336 cm^2/V-sec that we previously reported using stibine as a source of antimony (Ref. 11).

This method should also be useful for the growth of AlSb. In this case, an Al source would be substituted for the Ga source used here and the quartz tube would be protected by an alumina or carbon-foil liner.

III. CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated during this contract period that the vapor-phase growth system developed during earlier phases of this contract for the preparation of In- and Ga-containing III-V compounds can be suitably extended for the preparation III-V compounds containing Al. In the case of AlAs synthesized by this method, exceptional results have been achieved with regard to the electrical properties and chemical stability of this compound. This result, coupled with the previous successes for $GaAs_{1-x}P_x$, $InAs_{1-x}P_x$, and $GaAs_{1-x}Sb_x$ alloys, and GaN provides extensive evidence for the general excellence of this growth technique. In addition, the successful synthesis of single-crystalline epitaxial deposits of nine compounds, and representative compositions from six alloy series, demonstrates the versatility and compatibility of this system. With many of these compounds, n- and p-type doping, and the preparation of multilayer structures, have been achieved for the first time by vapor-phase growth.

Thus, virtually all of the objectives of this contract have been successfully accomplished. The demonstrated success of this research program has broad implications with regard to the utility of III-V compounds for device application.

Future work should involve providing further improvement in the purity and crystallinity of the Al-containing compounds, and in obtaining controlled n- and p-type doping of these materials. In addition, the synthesis of alloys of these compounds should be explored along with continued exploration of the $Ga_{1-x}In_xP$ alloy system. Finally, additional research should be carried out to provide reproducible and controlled p-type doping of GaN.

IV. NEW TECHNOLOGY APPENDIX

A. Title: Vapor Growth of AlAs

Page Reference: 4

Comments: AlAs and $Ga_{1-x}Al_xAs$ alloys are potential candidates for visible
electroluminescence diode materials, but growth problems
prevented the preparation of these materials as single-
crystalline vapor-grown layers. Single-crystalline AlAs layers
have now been prepared for the first time from the vapor phase
by preventing attack of the deposition apparatus and by placing
the aluminum-chloride outlet orifice within close proximity of
the substrate.

B. Title: AlAs p-n Junction Structures

Page Reference: 5

Comments: The utility of AlAs for high-temperature applications, or for
electroluminescence, would be greatly enhanced if stable p-n
junctions could be fabricated in this material in a reproducible
manner. Now, for the first time, it has been demonstrated that
stable p-n junctions can be prepared in vapor-grown AlAs.

C. Title: Ge-Acceptor Doping of Single-Crystal GaN

Page Reference: 19

Comments: The preparation of p-n junction structures in GaN requires that
the high inherent n-type impurities be compensated before a
conducting p-type sample can be achieved. Conducting p-type
GaN has been prepared for the first time by doping with Ge-
acceptor impurities.

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APPENDIX A

The Preparation and Properties of
Vapor-Deposited Single-Crystalline GaN

Abstract

Single-crystalline, colorless, GaN has been prepared by a vapor-phase growth technique previously used to prepare GaAs, GaP, and GaSb. These crystals are the first reported specimens of GaN suitable for good electrical and optical evaluation of this compound. It has been determined that GaN has a *direct* energy bandgap of 3.39 eV, and that undoped crystals prepared by this method have a very high, inherent electron concentration, typically above $10^{19}/cm^3$, which is probably related to a high density of nitrogen vacancies. Conducting *p-type* specimens have been prepared using Ge as the dopant; but this result has been difficult to reproduce, and the samples have been electrically inhomogeneous.

I. General

A large amount of work has been expended for the preparation and characterization of III-V compounds having bandgaps corresponding to the spectral range from the infrared to the middle of the visible spectrum. In general, this involves compounds formed from the group-V elements As, P, and Sb. In contrast, for the nitrogen-containing compounds which have relatively large bandgaps (extending through the visible and into the ultra-violet), very little work has been reported despite their potential for use as photoconductors, as both cathodo- and electroluminescent devices, and for high-temperature applications.

One nitride of particular interest is GaN since its bandgap corresponds to the edge of the ultra-violet and, therefore, could be applicable to the entire visible spectrum. The work that has been reported has in general described the preparation and properties of polycrystalline deposits, usually prepared by the reaction of NH_3 with Ga (Ref. A-1), Ga_2O_3 (Ref. A-2), or GaP (Ref. A-3). The only report of single-crystalline material involves small needles, only a few microns in length (Ref. A-4). It is significant that very little reported work deals with the growth of GaN from the vapor phase. In contrast, vapor-phase growth techniques have played an important role in the preparation and characterization of GaAs (Ref. A-5), GaP (Ref. A-6), and GaSb (Ref. A-7). In particular, a compatible method (Refs. A-7 and A-8) has been developed for the preparation of these compounds in which the respective hydrides AsH_3, PH_3, and SbH_3 serve as the sources of the group-V elements, and Ga is transported as its subchloride via a reaction with HCl gas. This technique has now been further extended for the preparation of GaN by using NH_3 as the source of nitrogen.

The apparatus used in this study is essentially identical to that described previously (Ref. A-8), with the exception that NH_3 is used in place of the other group-V hydrides. It is primarily comprised of a straight tube

through which the pertinent gaseous species flow to provide chloride-transport of metallic gallium, and subsequent reaction of these transport-products with ammonia to form GaN on a substrate surface.

With the exception of the ammonia* and <0001>-oriented sapphire single-crystalline substrates**, the materials employed in this study are as described previously (Ref. A-8). The sapphire substrates were mechanically polished** to a flat mirror-smooth finish, and then heat-treated in hydrogen at 1200°C prior to their introduction to the growth apparatus. Typical substrate dimensions were about 2 cm^2 in area and about 0.25-mm thick.

The growth procedure also closely follows that described previously (Ref. A-8). Freshly heat-treated substrates are inserted into the deposition zone of the growth chamber and heated in hydrogen at a rate of about 20°C/min. When the final growth temperature is reached, the NH_3 flow is started and, after a 15-min period to allow the NH_3 concentration to reach a steady-state value, the HCl flow is started to provide transport of the Ga and deposition of GaN.

The flow rates of pure HCl and NH_3 are about 5 and 400 cm^3/min, respectively, and an additional 2.5 liters/min of hydrogen are used as a carrier gas. With these flow rates, a substrate temperature of 825°C, a Ga-zone temperature of 900°C, and a center zone (that region between the Ga-and deposition-zones) temperature of 925°C, growth rates of about 0.5 μm/min are obtained under steady-state conditions. Typical thicknesses for these deposits have been in the range of 50 to 150 μm. Doping is accomplished, during the growth process, by introducing the dopant to the growth apparatus either as its hydride or by direct evaporation of the element into a hydrogen carrier gas.

X-ray analysis by the Debye-Scherrer technique indicates that these layers are single-phase, hexagonal GaN. having the wurtzite structure and lattice parameters a = 3.189 Å, c = 5.185 Å, at room temperature. The lattice parameter is presented as a function of temperature in Figure A-1 for the range of 300° to 900°K. These data were obtained by means of powder patterns taken every 100°K with a Unicam high-temperature camera. From these data, a mean coefficient of thermal expansion for the a-direction is determined to be 5.59 x 10^{-6}/°K for the entire temperature range investigated, while for the c-direction, values of 3.17 x 10^{-6} and 7.75 x 10^{-6}/°K are approximated for the temperature ranges 300° to 700°K and 700° to 900°K, respectively. Laue back-reflection patterns show this material to be single-crystalline and epitaxial, having a <0001> orientation.

The GaN prepared by this technique was found to be insoluble in H_2O, acids, or bases at room temperature. It dissolves slowly in hot alkalis; a sample weighing 150 mg takes 24 hours to completely dissolve in boiling NaOH. Emission-spectrographic and mass-spectrometric analyses indicate a total impurity content of less than 10 ppm and less than 1 ppm of any one impurity.

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*   from Scientific Gas Products, Edison, New Jersey
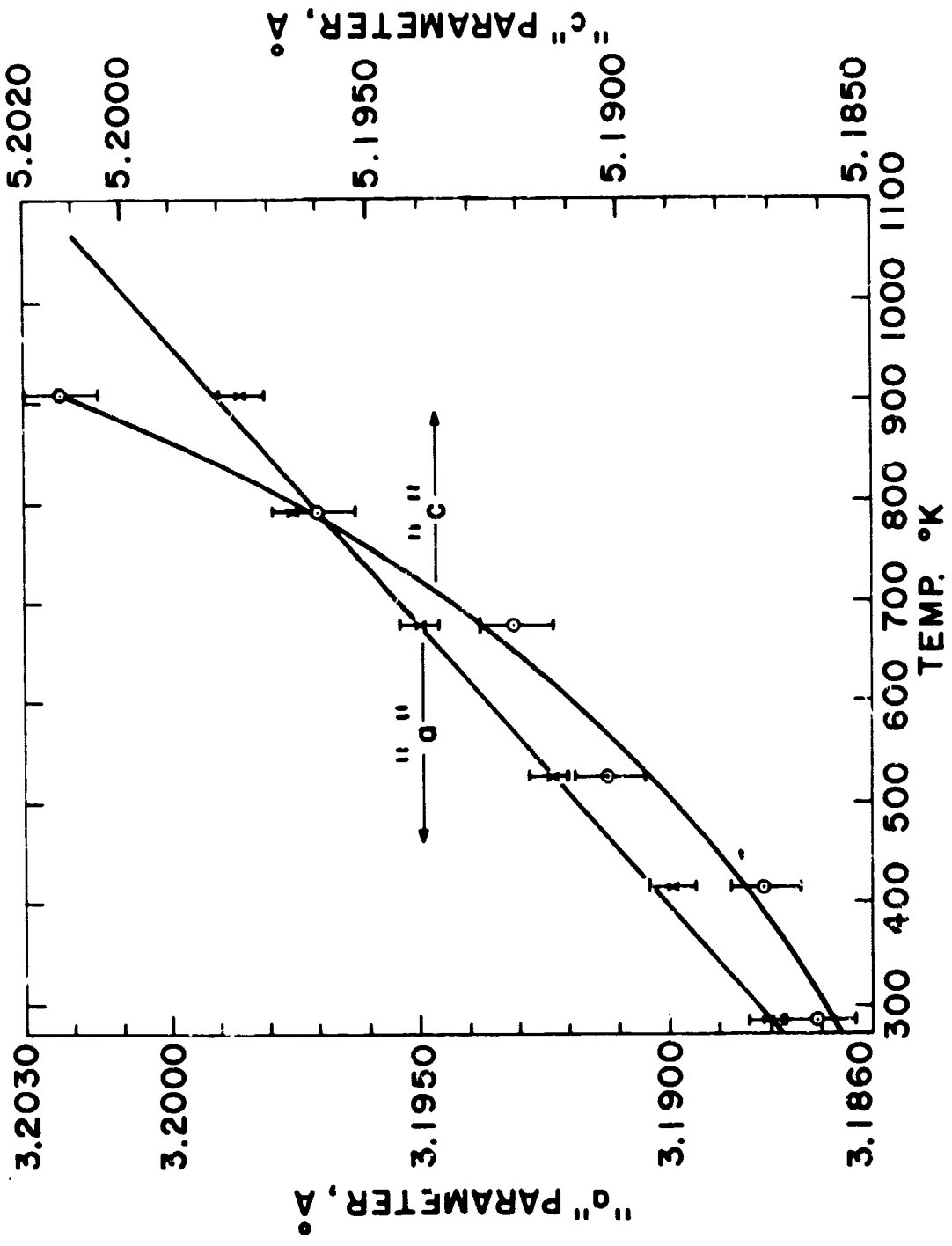**   from Insaco, Quakerstown, Pennsylvania

Figure A-1. The dependence on temperature of the lattice parameters of GaN.

Room-temperature, optical-absorption measurements on undoped GaN reveal a very-sharp absorption edge, as shown in Figure A-2, and on the high-energy side of this edge the absorption coefficient obeys the general relationship

$$\alpha = \alpha_o (E - E_g)^n$$

where E is the photon energy, and E_g is the energy of the bandgap (Ref. A-9). From the absorption data, E_g and n were determined to be 3.39 eV and 0.62, respectively. The value of 0.62 is indicative of a *direct* transition across the energy gap and is consistent with values obtained for other direct bandgap III-V compounds (Ref. A-10). The value for E_g of 3.39 eV obtained in this study is slightly larger than the previously reported value of 3.26 eV (Ref. A-11).

These epitaxial layers were examined by conventional Hall coefficient and resistivity measurements. Undoped samples are n-type, having typical electron concentrations in the range of 1 to 5 x 10^{19}/cm^3 and room-temperature mobilities of between 125 and 150 cm^2/V-sec. These high mobility values for such high carrier concentrations also support the contention that GaN is a direct bandgap semiconductor. Since the total impurity content of these crystals is at least two orders of magnitude too low to account for the high inherent, donor concentration it is suspected that the donor is related to a native defect, probably a nitrogen vacancy. In this regard, it should be noted that GaN dissociates to liberate nitrogen at temperatures as low as 600°C (Ref. A-2).

Preliminary experiments have been carried out in an effort to dope these GaN layers with acceptor impurities. The impurities studied to date include Zn, Mg, Hg, Si, and Ge. Both Zn and Mg produce high-resistivity material ($\rho > 10^9$ Ω cm) and color the normally colorless GaN orange and yellow, respectively. Evidently, both of these impurities are introduced as deep acceptor states. Hg-doped samples remained highly conducting n-type, undoubtedly due to a relatively limited solubility of Hg in GaN at the growth temperature. Emission spectrographic analysis revealed that Hg had not been incorporated in the GaN in concentrations greater than 30 ppm.

Consistent with the hypothesis that these GaN layers have a very high density of nitrogen vacancies, the group IV elements, Si and Ge, are attractive candidates as p-type dopants since they are readily introduced to the growth apparatus in the form of their hydrides, and as substitutes for nitrogen sites should behave as acceptor states. Indeed, the best success was achieved with these impurities. In the case of Si, substantial compensation was achieved without introducing a color to the GaN indicating that Si is probably a shallow acceptor. However, to date, although the carrier concentration has been reduced to as low as 3 x 10^{16}/cm^3, Si-doped samples have all been n-type.

With Ge-doping, conducting p-type behavior has been achieved. Two layers have been prepared with resistivities of 0.01 and 0.94 Ω-cm for hole concentrations of 6 x 10^{19} and 6 x 10^{18}/cm^3, respectively. While this result is encouraging since it demonstrates that a fundamental mechanism does not exist which prevents amphoteric doping of this compound, it has been very difficult to reproduce and the layers are non-uniform, with some regions of the sample being n-type.
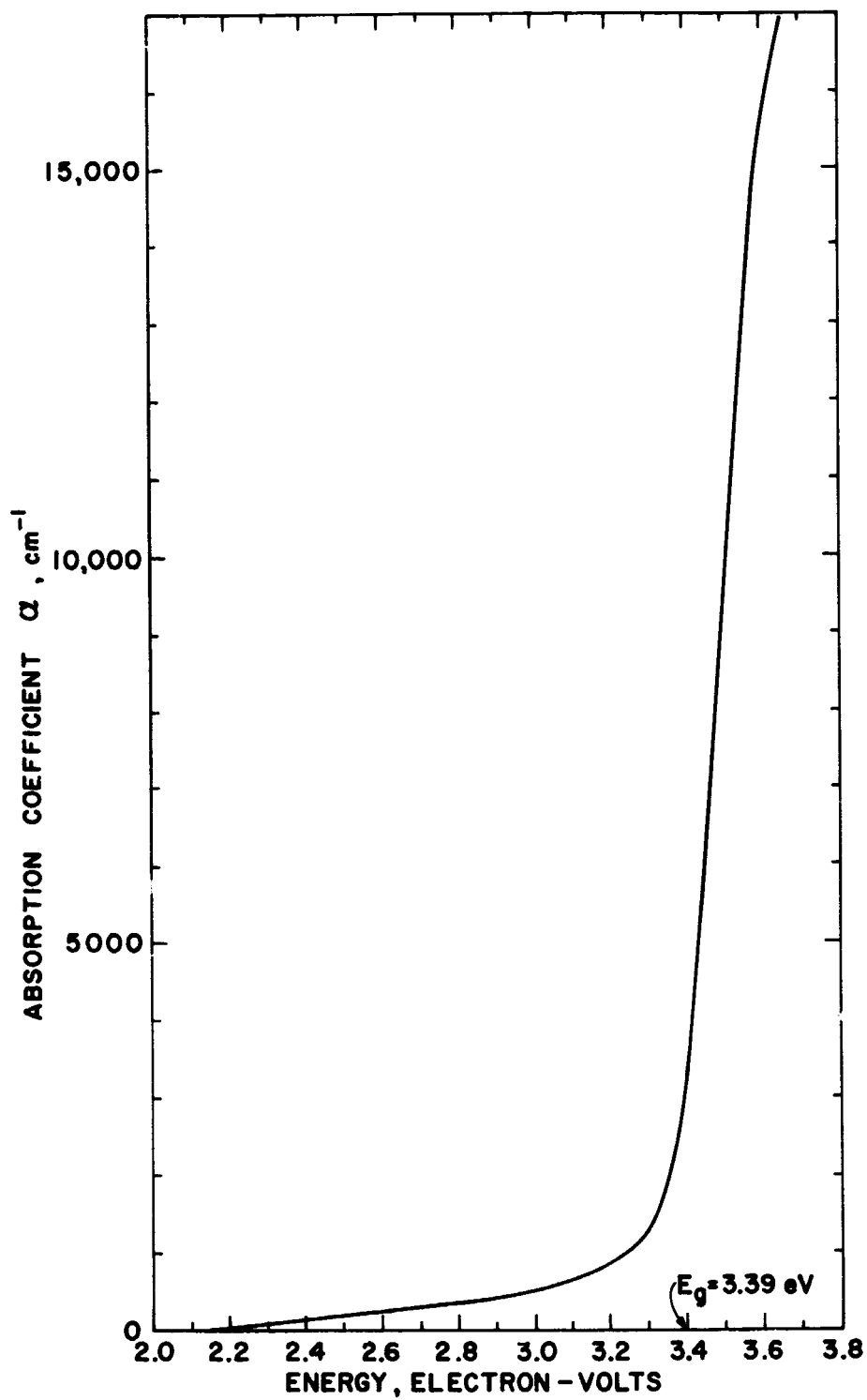
Figure A-2. The dependence of the absorption coefficient on energy for GaN.

This aspect of the research on GaN will be continued to provide a more detailed description of the role of acceptor impurities in this compound, and will be the subject matter of a latter publication.

II. Acknowledgments

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APPENDIX B

Thermochemistry of the Vapor Growth of AlAs

I. Introduction

The application of equilibrium thermodynamics to flow-through-systems has been discussed by Jeffes (Ref. B-1), Goodeve (Ref. B-2), and Mandel (Ref. B-3) among others. It is frequently possible to apply equilibrium thermodynamics since for most gas-phase reactions the activation energies lie between 25 and 75 kcal/mole, and, therefore, above 500°C the reaction rates are so fast that chemical kinetics no longer become rate determining. Furthermore, if the mass transport is controlled by the flow conditions, then equilibrium thermodynamics is the dominant factor and may be used to describe the system.

The thermodynamic treatment presented here is based primarily on the following assumptions:

1. The chemical species proposed are present in the chemical reactions.

2. The reactions between the chemical species are known and the thermochemical data chosen to describe the species are sufficiently accurate.

3. The condition of thermodynamic equilibrium can be used to describe the system; that is, the rate of deposition is not kinetically controlled by a solid-gas phase interface reaction or by heat transfer between the gas species and their surroundings.

Even if the condition of equilibrium are not met, a consideration of the equilibrium thermodynamics of the system gives a good understanding of the predominant gas species and the reactions between them. This is particularly useful in predicting the effects of various growth variables such as temperatures, temperature gradients, and gas-flow rates on the feasibility and efficiency of a mass-transport process.

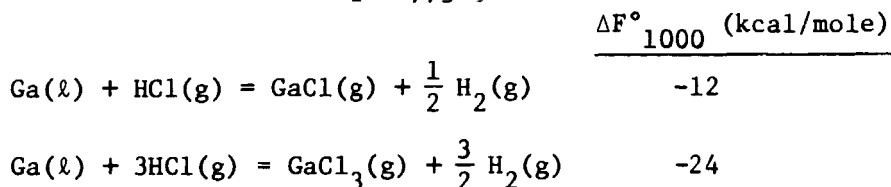### II. Comparison Between Gallium Arsenide and Aluminum Arsenide Vapor Transport

The conditions for vapor growth of gallium arsenide have been well established. By comparison of the energetics of the respective reactions with the corresponding ones in the aluminum-arsenide system, it may be possible to determine growth conditions which are appropriate for good growth of aluminum arsenide.

A. The Gallium Arsenide System

The reactions which are generally believed to be responsible for mass transport of gallium arsenide are the following:

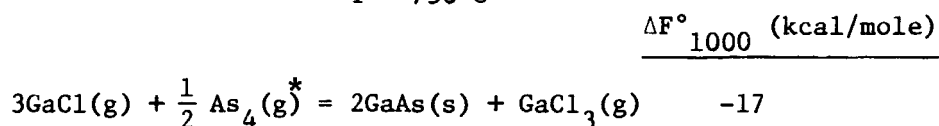Gallium Zone:

<div align="center">T $\sim$ 775°C</div>

$$\Delta F^{\circ}_{1000} \text{ (kcal/mole)}$$

$$Ga(\ell) + HCl(g) = GaCl(g) + \frac{1}{2} H_2(g) \qquad -12$$

$$Ga(\ell) + 3HCl(g) = GaCl_3(g) + \frac{3}{2} H_2(g) \qquad -24$$

Since both reactions have negative-free energies, both the monochloride and trichloride will be present. However, in the presence of free gallium another raction can take place, namely,

$$\Delta F^{\circ}_{1000} \text{ (kcal/mole)}$$
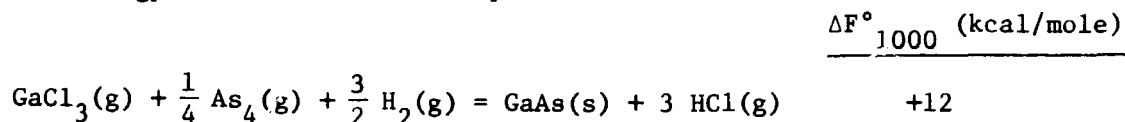
$$GaCl_3(g) + 2Ga(\ell) = 3GaCl(g) \qquad -11$$
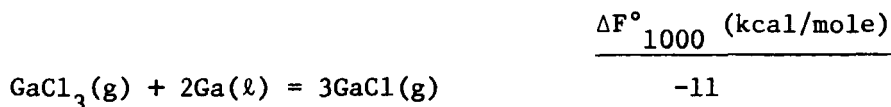
The negative-free energy indicates that although the monochloride and trichloride can form at the experimental temperatures, the primary gas-phase species in the presence of free gallium under equilibrium conditions is the monochloride. This is in agreement with experimental findings in which the correlation between the number of moles of Ga(ℓ) and of HCl(g) consumed is close to 1:1.

Deposition Zone:

<div align="center">T $\sim$ 750°C</div>

$$\Delta F^{\circ}_{1000} \text{ (kcal/mole)}$$

$$3GaCl(g) + \frac{1}{2} As_4(g)^* = 2GaAs(s) + GaCl_3(g) \qquad -17$$

The reaction shows that gallium monochloride reacts with the arsenic to form the epitaxial gallium arsenide. Even if the trichloride is not converted to the monochloride in the presence of free gallium due to kinetic considerations, gallium trichloride does not lead to the deposition of gallium arsenide since the free energy for the reaction is positive.
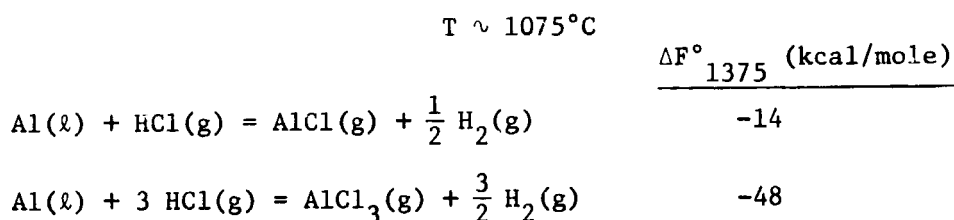
$$\Delta F^{\circ}_{1000} \text{ (kcal/mole)}$$

$$GaCl_3(g) + \frac{1}{4} As_4(g) + \frac{3}{2} H_2(g) = GaAs(s) + 3 HCl(g) \qquad +12$$

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* $As_4(g)$ is the predominant specie at the temperature used for the growth of GaAs.
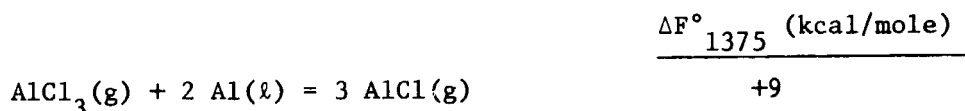
B. The Aluminum Arsenide System

The corresponding reactions in the aluminum-arsenide system are presented below.

Aluminum Zone:

$$T \sim 1075°C$$

$$\Delta F°_{1375} \ (kcal/mole)$$

$$Al(\ell) + HCl(g) = AlCl(g) + \frac{1}{2} H_2(g) \qquad -14$$

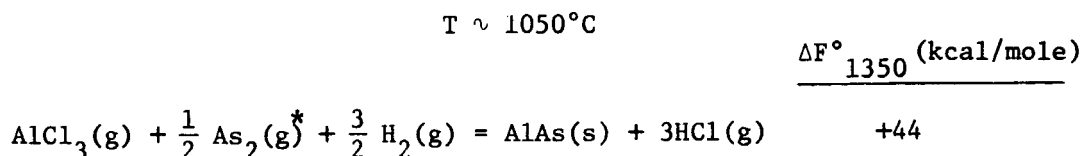$$Al(\ell) + 3 HCl(g) = AlCl_3(g) + \frac{3}{2} H_2(g) \qquad -48$$

Since the free energies for both reactions are negative, both the monochloride and trichloride should be formed. However, in the presence of free aluminum, the following reaction must be considered:

$$\Delta F°_{1375} \ (kcal/mole)$$

$$AlCl_3(g) + 2 Al(\ell) = 3 AlCl(g) \qquad +9$$

Therefore, the predominant species in the aluminum zone under equilibrium conditions is the trichloride. This is in direct contrast with the gallium zone in the gallium-arsenide system where the *monochloride* is the predominant species.

Deposition Zone:

$$T \sim 1050°C$$

$$\Delta F°_{1350} \ (kcal/mole)$$

$$AlCl_3(g) + \frac{1}{2} As_2(g)^* + \frac{3}{2} H_2(g) = AlAs(s) + 3HCl(g) \qquad +44$$
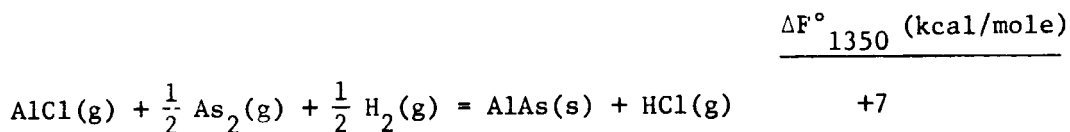
It can be seen from this reaction that if only the trichloride is present, there should be no deposition of aluminum arsenide. The presence of only $AlCl_3(g)$ was postulated on the basis of complete *equilibrium* established in the aluminum zone. If, however, equilibrium is not established in the aluminum zone due to kinetic considerations, the reaction between the monochloride and arsenic vapor can take place.
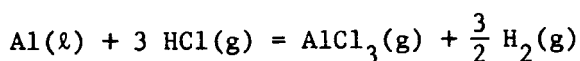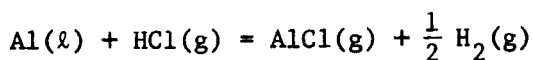
$$\Delta F°_{1350} \ (kcal/mole)$$

$$3 AlCl(g) + As_2(g)^* = 2 AlAs(s) + AlCl_3(g) \qquad -18$$

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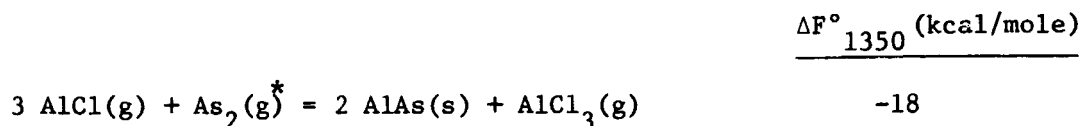
* $As_2(g)$ is the predominant specie at the temperature used for the growth of AlAs.

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The reaction of the monochloride with arsenic must result in aluminum arsenide and aluminum trichloride As products since the other alternative reaction does not take place, namely,

$$\Delta F^{\circ}_{1350} \ \text{(kcal/mole)}$$

$$\text{AlCl(g)} + \frac{1}{2} \text{As}_2(g) + \frac{1}{2} \text{H}_2(g) = \text{AlAs(s)} + \text{HCl(g)} \qquad +7$$

### III. Further Considerations of Reactions in the Aluminum-Arsenide Vapor Growth

In Figure B-1 the free energies of reaction as a function of temperature are given for possible reactions for the aluminum arsenide vapor-growth process. Based on the best presently available data (Refs. B-5 through B-8) it can be seen that for the reactions

$$\text{Al}(\ell) + \text{HCl(g)} = \text{AlCl(g)} + \frac{1}{2} \text{H}_2(g)$$

$$\text{Al}(\ell) + 3 \text{HCl(g)} = \text{AlCl}_3(g) + \frac{3}{2} \text{H}_2(g)$$

ΔF° is negative over the entire temperature range which would be considered for vapor growth. But for the reaction

$$\text{AlCl}_3(g) + 2\text{Al}(\ell) = 3 \text{AlCl(g)}$$
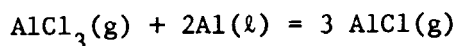
ΔF° is positive below about 1520°K and negative above 1520°K. Therefore, under *equilibrium* conditions $\text{AlCl}_3(g)$ is the primary product below 1520°K. Also, since the free energy for the reaction

$$\text{AlCl}_3(g) + \frac{1}{2} \text{As}_2(g) + \frac{3}{2} \text{H}_2(g) = \text{AlAs(s)} + 3\text{HCl(g)}$$
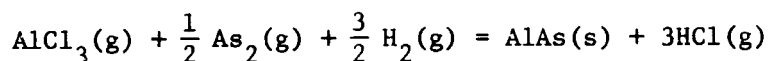
is positive over all temperatures and for the reaction

$$3\text{AlCl(g)} + \text{As}_2(g) = 2\text{AlAs(s)} + \text{AlCl}_3(g)$$
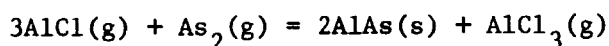
is negative *only* for temperatures *below* 1520°K and for the reaction

$$\text{AlCl(g)} + \frac{1}{2} \text{As}_2(g) + \frac{1}{2} \text{H}_2(g) = \text{AlAs(s)} + \text{HCl(g)}$$
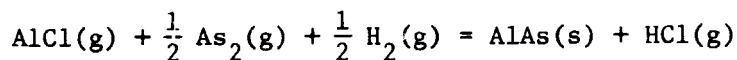
is positive for temperatures above 1200°K, there should be no deposition of aluminum arsenide at all if equilibrium is established.
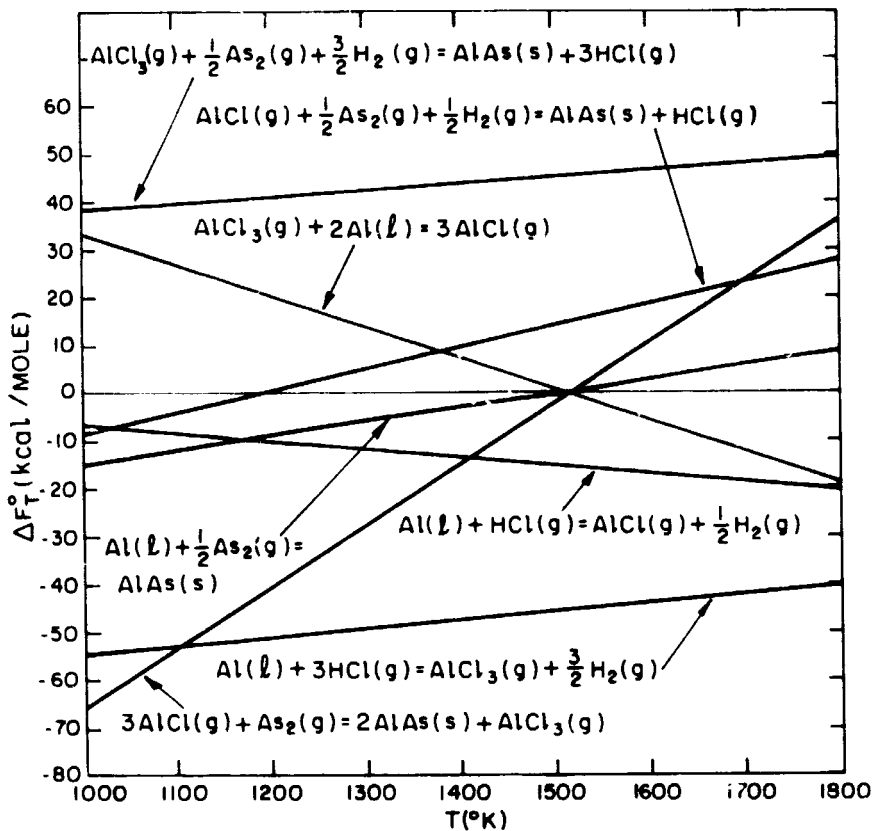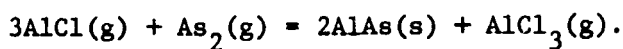
Figure B-1. Free energy as a function of temperature for reactions involving Al chlorides.

A temperature gradient could be used such that the aluminum zone is kept above 1520°K to form the monochloride and the deposition zone below 1520°K to cause reaction of the monochloride with arsenic according to

$$3AlCl(g) + As_2(g) = 2AlAs(s) + AlCl_3(g).$$

Even if the monochloride re-equilibrates with the trichloride at the lower temperature of deposition, free aluminum is liberated according to the reaction
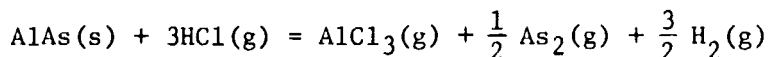
$$3AlCl(g) = 2Al(\ell) + AlCl_3(g)$$
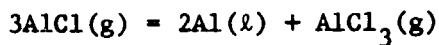
which can react with the arsenic vapor

$$Al(\ell) + \frac{1}{2} As_2(g) = AlAs(s).$$

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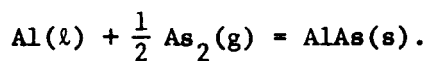
Another feature can be seen from Figure B-1. In principle it should be possible to remove any deposit of AlAs(s) simply by reaction with HCl(g) according to the reaction
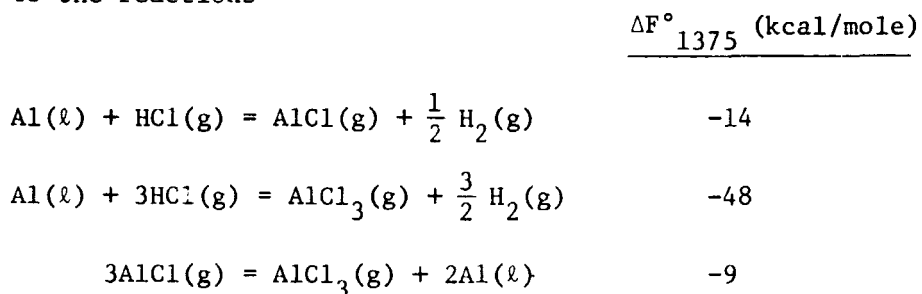
$$AlAs(s) + 3HCl(g) = AlCl_3(g) + \frac{1}{2} As_2(g) + \frac{3}{2} H_2(g)$$

since the $\Delta F°$ is in the order of -40 to -50 kcal/mole. The use of HCl cleaning has been experimentally demonstrated, and should be particularly useful where moisture presents a serious contamination problem.

IV. Non-Equilibrium Considerations

The thermodynamic treatment presented above is based on the assumption that *equilibrium* is established throughout the system, and has led to the conclusion that deposition should not occur at temperatures below 1520°K without the use of a temperature gradient where the hot zone is above 1520°K. This is in direct conflict with experimental findings. It is therefore of interest to consider non-equilibrium effects which lead to deposition.

One of the primary factors which pushes the system from equilibrium leading to deposition of aluminum arsenide is variation in the flow rate for a fixed HCl/H_2 dilution through the aluminum zone. At relatively low flow rates where the system approaches equilibrium, primarily $AlCl_3(g)$ is formed according to the reactions

$$\Delta F°_{1375} \text{ (kcal/mole)}$$

$$Al(\ell) + HCl(g) = AlCl(g) + \frac{1}{2} H_2(g) \qquad -14$$

$$Al(\ell) + 3HCl(g) = AlCl_3(g) + \frac{3}{2} H_2(g) \qquad -48$$

$$3AlCl(g) = AlCl_3(g) + 2Al(\ell) \qquad -9$$

Under these conditions no deposition occurs. At high HCl/H_2 flow rates where non-equilibrium effects start to appear, the reaction to form the monochloride would kinetically dominate since it is a bimolecular reaction whereas the reaction to form the trichloride from the aluminum is a trimolecular reaction. Also, at high HCl/H_2 flows the monochloride would be swept from the aluminum zone to the deposition zone before equilibrium is established to convert the monochloride to the trichloride. These conditions lead to deposition. At very high flow rates a fraction of HCl(g) passes through the aluminum zone unreacted. The HCl(g) competes with the deposition reaction since HCl(g) can react with aluminum arsenide to etch the deposit.
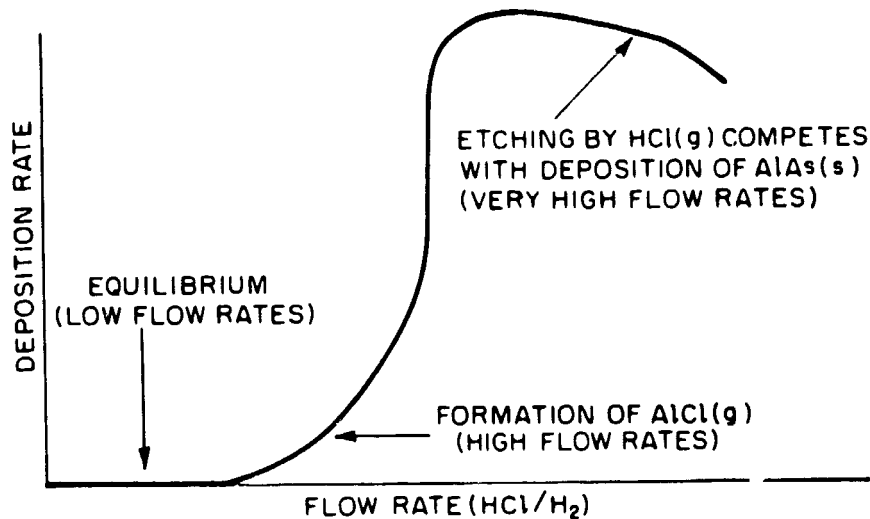
$$\Delta F°_{1350} \text{ (kcal/mole)}$$

$$AlAs(s) + 3HCl(g) = AlCl_3(g) + \frac{1}{2} As_2(g) + \frac{3}{2} H_2(g) \qquad -44$$
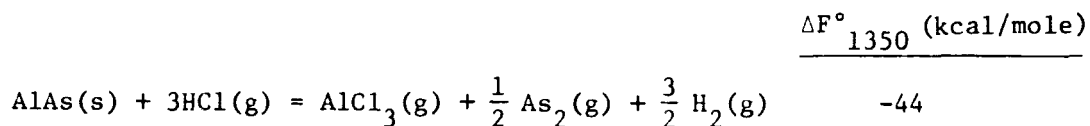
Figure B-2. Predicted AlAs-deposition rate as a function of flow rate for a fixed HCl/H$_2$ ratio.

Therefore, for a fixed HCl/H$_2$ dilution, the following variation of deposition rate on HCl/H$_2$ flow rate may be expected, as shown in Figure B-2.

V. Summary and Conclusions

(1) The thermochemistry of the vapor-phase crystal growth of aluminum arsenide is not significantly different from that of gallium arsenide. The decisive difference is that under equilibrium at the respective experimental temperatures, the predominant gas-phase species in the gallium zone is GaCl(g) and in the aluminum zone is AlCl$_3$(g).

(2) Only AlCl(g) and *not* AlCl$_3$(g) leads to vapor deposition of AlAs(s).

(3) The experimental findings of Richman (Ref. B-4) that the ratio of HCl(g) to Al(ℓ) is 1:1 at temperatures of around 1800°K and of Dreeben who fou.d values greater than 1:1 are now reconciled on the basis of the temperature dependence of the equilibrium between AlCl(g) and AlCl$_3$(g) and the possible deviation from equilibrium in the reactions of the HCl(g) with aluminum in the aluminum zone.

(4) HCl etching of aluminum arsenide has been predicted from free energies of reaction and has been experimentally demonstrated. This should be a useful technique for cleaning reaction tubes where a wet-chemical cleaning presents a serious contamination problem.

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