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

by

J. J. Tietjen, R. Clough, and D. Richman

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Princeton, New Jersey

Electronics Research Center
Cambridge, Massachusetts
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

The vapor phase growth technique has now been extended to the preparation of single crystalline $In_{1-x}Ga_xP$ alloys. This represents the first time these alloys have been prepared from the vapor phase. In addition, improvements in the preparation of $In_{1-x}Ga_xAs$ alloys have been realized, and controlled n- and p-type doping of InAs has been achieved.

Thus, the main objectives for the first year of the contract have been achieved, namely the growth of single crystalline GaAs, GaP, GaSb, InAs, InP, and alloys of $GaAs_{1-x}P_x$, $GaAs_{1-x}Sb_x$, $InAs_{1-x}P_x$, $In_{1-x}Ga_xAs$, and $In_{1-x}Ga_xP$, over wide composition ranges. Despite the great breadth of this work, the electrical properties of these materials have equalled or exceeded the state-of-the-art. Furthermore, n- and p-type doping and multilayer structures have been prepared in a variety of these materials. Also, the effect of strain on lowering the carrier mobilities has been delineated.

Only the preparation of InSb as a primary objective has not been realized. However, in general, the antimonide phase of this research has been severely restricted because of difficulties related to obtaining an adequate supply of stibine gas. Therefore, in the next quarter, the preparation of InSb will be emphasized, and research on the $GaAs_{1-x}Sb_x$ system will be completed.

I. INTRODUCTION

The primary objective of this contract, during the first four quarters, was to develop a compatible vapor phase growth method for the preparation of GaAs, GaP, GaSb, InAs, InP, InSb, and selected alloys of these compounds. In addition, the method was to permit n- and p-type doping and the preparation of multilayer structures.

Three separate growth systems have been used in this study, which has permitted efficient optimization of the growth parameters pertinent to these various materials. As a result, during the first three quarters, all of the above compounds have been grown, with the exception of InSb; and alloys of $GaAs_{1-x}P_x$, $InAs_{1-x}P_x$, $GaAs_{1-x}Sb_x$, and $In_{1-x}Ga_xAs$ have been prepared. Emphasis was placed on not only achieving single crystalline growth, but also on achieving high purity, which was obtained. In addition, n- and p-type doping and the preparation of multilayer structures has been achieved with selected materials. Thus, the ability of the vapor phase growth method being developed to fulfill the need of this program has been demonstrated.

During the fourth quarter, $InAs_{1-x}P_x$ alloys have been more completely characterized, and controlled n- and p-type doping of InAs has been achieved. Improved control of the composition of $In_{1-x}Ga_xAs$ alloys has been obtained, and an $In_{.42}Ga_{.58}As$ alloy has exhibited electrical properties exceeding the best ever published. In addition, for the first time, $In_{1-x}Ga_xP$ alloys have been prepared from the vapor phase, and initial characterization indicates that these alloys have direct energy band gaps in excess of 2.0 eV, which has important implications for visible electroluminescence.

Due to manufacturer's delays, and an unexpected depletion of the stibine supply, the antimonide phase of this research has been severely restricted. As a result, InSb has not yet been prepared, but work on this compound will commence during the next quarter.

II. TECHNICAL DISCUSSION

A. Growth of InAs, InP, and $InAs_{1-x}P_x$ Alloys

The preparation and electrical evaluation of $InAs_{1-x}P_x$ has been extended to provide more complete characterization of the electron mobility in this alloy series. As shown in Table I, the mobility values continue to be high for arsenic-rich compositions at room temperature and for all compositions at low temperatures. However, the room temperature values are comparatively low for phosphorus-rich specimens. This is most likely due to excessive crystal strain, as indicated by irregularities observed upon cleaving phosphorus-rich samples. In addition, the general crystallographic perfection of the phosphorus-rich alloys seems to be reduced since their surfaces contain a high density of macroscopic hillocks which are not seen with arsenic-rich compounds. These problems should be alleviated by increased compositional grading between the InAs substrate and the final alloy composition.

An additional cooled-substrate holder has been fabricated which is similar in construction to that previously described in Quarterly Technical Report No. 3, except that the substrate is oriented 45° to the gas flow instead of being parallel. This permits more of the vapor phase constituents to impinge on the substrate surface and thus facilitates more rapid growth. Using this substrate holder and thicker graded regions, the properties of InP have continued to improve. As shown in Table I, sample no. P-22-68-P has an electron concentration below the $10^{16}/cm^3$ range, and a mobility of 16,800 cm^2/V-sec at 77°K, which is equivalent to the best reported in the literature at this carrier level. Again, the room-temperature mobilities are low, and it is believed this is also related to crystal strain.

Results for the growth of InP on InAs are shown in Table II. Here steep temperature gradients were used to drive the disproportionation reaction. As expected, in general it was found that growth rates improved by orienting the substrate 45° to the gas flow as compared with the parallel orientation. With the exception of a few cases, however, the surfaces were rough and covered with hillocks, and it is evident that an even thicker graded region or growth on pre-grown InP substrates is required for the continued improvement of electrical properties.

Doping of InAs has been further investigated using hydrogen-selenide gas as a source of selenium for n-type doping, and zinc vapor for p-type. The results are shown in Table III. The selenium-doped layers exhibit mobilities comparable to those reported in the literature for untreated samples, namely about 10,000 cm^2/V-sec at $1x10^{18}$ cm^{-3}, as is also characteristic of undoped InAs prepared by this technique. Thus, doping to these high donor concentrations does not degrade the material. For p-type doping, a minimum source temperature of 375°C is needed to overcompensate the background donor concentration; but, otherwise, doping with zinc is straightforward and good electrical properties are obtained.

TABLE I

Electrical Properties of $InAs_{1-x}P_x$ Compounds

Sample No.	x	Net Carrier Conc., cm^{-3} at 300°K	Net Carrier Conc., cm^{-3} at 77°K	Electron Mobility, $cm^2/V\text{-}sec$ at 300°K	Electron Mobility, $cm^2/V\text{-}sec$ at 77°K
1-10-68-M	0.15	2.8×10^{16}	1.9×10^{16}	12,200	30,000
12-18-67-M	0.48	5.5×10^{15}	1.6×10^{15}	4,060	24,500
1-18-68-M	0.61	4.4×10^{16}	--	2,920	--
2-1-68-M	0.62	3.2×10^{16}	1.8×10^{16}	3,120	13,400
12-27-67-C	1.00	5.2×10^{15}	3.2×10^{15}	2,470	9,600
1-22-68-P	1.00	8.5×10^{15}	3.5×10^{15}	2,030	16,800

TABLE II

Preparation of InP Using Cooled-Substrate-Holder

Sample No.	Substrate Orientation, Degrees[a]	Temperatures,[c] °C Substrate	ΔT[c]	Growth Rate, Microns/hr.	Comments
2-8-68-P3	45	400	450	13	
2-9-68-P	45	450	350	28	
2-12-68-P	45	450	350	22	
2-8-68-P2	45	450	400	<32	
2-14-68-P1	0	500	300	12	
2-15-68-P	45	500	300	37	
2-16-68-P	45	500	300	12	32 microns graded region; surface covered with hillocks
2-20-68-P	45	550	350	40	
2-7-68-P3	45	550	300	19	Shiny surface
2-7-68-P2	45	600	250	16	
1-3-68-M	0	650	650[d]	4	PH_3 flow, 80 cc/min
2-7-68-P1	45	650	200	6	
2-2-68-P2	0	650	250	12	
12-26-67-C	0	675	50	13	
1-22-68-P	0	675	50	15	
12-27-67-C	0	675	50	40	
1-30-68-P	0	700	50	9	
1-31-68-P	0	700	100	10	
2-1-68-P	0	700	150	6	
2-6-68-P1	45	700	150	10	
2-6-69-P2	0	700	150	10	

Notes:

a. Angle between substrate surface and flow direction
b. Flow rates: H_2 carrier gas for PH_3, 800 cc/min
H_2 carrier gas for HCl, 300 cc/min
HCl, 4.0 cc/min
PH_3, 40 cc/min
c. Temperatures: Center furnace, 975°C
Indium furnace, 950°C
ΔT is difference between growth furnace temperature and substrate temperature, °C
d. Indium furnace, 850°C

TABLE III

Electrical Properties of Se- and Zn-doped InAs

Sample No.	Dopant	Type	Net Carrier Conc., cm^{-3} at 300°K	Net Carrier Conc., cm^{-3} at 77°K	Hall Mobility, $cm^2/V\text{-sec}$ at 300°K	Hall Mobility, $cm^2/V\text{-sec}$ at 77°K
2-15-68-M	Se	n	1.2×10^{18}	1.2×10^{18}	10,000	10,600
2-6-68-M	Se	n	3.1×10^{19}	--	1,470	--
2-20-68-M	Zn (300°C)*	n	9.2×10^{15}	6.2×10^{15}	21,500	90,000
2-26-68-M	Zn (350°C)	n	4.3×10^{15}	--	2,700	--
3-4-68-M	Zn (362°C)	n	4.0×10^{16}	3.2×10^{16}	464	1,560
2-29-68-M	Zn (375°C)	p	4.4×10^{17}	1.5×10^{17}	150	685
2-9-68-M	Zn (400°C)	p	7.2×10^{18}	7.1×10^{18}	91	58

* Numbers in parenthesis indicate the temperature of the zinc source.

The facility to grow $InAs_{1-x}P_x$ multilayer structures was demonstrated by preparing an n^+-n-p alloy structure on an InAs substrate. This consisted of a selenium-doped n^+-region graded in composition to $InAs_{.44}P_{.56}$, followed by a 10-micron-thick undoped $InAs_{.44}P_{.56}$ region, and terminated with a 1-micron-thick Zn-doped layer. The approximate carrier concentrations of the three regions are respectively, $n^+ = 1x10^{18}/cm^3$, $n = 1x10^{16}/cm^3$, and $p = 2x10^{17}/cm^3$. This specimen has been submitted to the Contract Monitor.

B. Growth of $In_{1-x}Ga_xAs$ Alloys

Previously, control of the composition of these alloys was provided by adjusting the temperatures of the In and Ga sources in order to regulate the relative vapor concentrations of InCl and GaCl. However, with this technique it is difficult to obtain alloys containing more than about 20% InAs since even at Ga temperatures as low as 700°C effective reduction of the GaCl concentrations is not achieved. This problem has now been solved by using the HCl dilution bulb (which is provided in the growth apparatus) to accurately control the concentration of HCl passing over the Ga and, thereby, reduce the GaCl concentration. In this way it has been possible to grow alloys containing up to 67% InAs, and no restriction on choice of composition is foreseen.

Using this method to control the alloy composition, an 8-mil-thick layer of $In_{.42}Ga_{.58}As$ has been prepared as an unsupported and, therefore, unstrained specimen. It has an electron carrier concentration of $7x10^{16}/cm^3$ with mobilities of 5,100 and 9,200 cm^2/V-sec at 300 and 77°K, respectively. These results are better than previously published values,[1] and are equivalent to those shown in the Final Report of a three-year study of these alloys.[2]

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

Work has been started on the $In_xGa_{1-x}P$ alloy system. Initially, we are concerned with establishing the temperature and flow conditions which yield reasonable growth rates across the entire alloy system.

Two alloy compositions have been grown on sapphire substrates in order to quickly determine the band gap-composition relationship. These layers were polycrystalline. Results of the x-ray and optical absorption experiments are shown in Table IV.

Table IV.

Physical Properties of $In_{1-x}Ga_xP$ Alloys

Sample No.	Lattice Constant (Å)	Band GaP (eV)	Composition (%GaP)
1	5.763	1.51	28
2	5.621	2.18	57

The composition was obtained by assuming Vegard's law of solid solutions.

Several single crystal layers of $In_xGa_{1-x}P$ have been grown on GaAs substrates. The procedure used was to start by growing GaAs, grading to GaP, and then grading again to $In_xGa_{1-x}P$. Two of these samples were thick enough to make Hall samples. The room-temperature data, together with the band gap as determined by optical absorption measurements, are presented in Table V.

Table V.

Energy Band Gap and Electrical Properties of $In_{1-x}Ga_xP$ Alloys at Room Temperature

Sample No.	Band GaP (eV)	Electron Concentration (cm^{-3})	Mobility (cm^2/V-sec)
3	1.88	$5x10^{17}$	650
4	2.12	$1.5x10^{17}$	92

From the sharpness of the absorption edges, along with the relatively high mobility of sample no. 3, it is inferred that these crystals have direct energy band gaps. This makes these materials particularly interesting for electroluminescent application in the visible region of the spectrum.

The repeated evidence for contamination of recent samples of these alloys, as indicated by the high carrier concentrations, as well as of the last $In_xGa_{1-x}As$ alloys, has been traced to a leak in the quartz reaction tube. This has now been replaced by a new tube.

In order to achieve high growth rates in this system, it was necessary to lower the total gas flow. This has now led to some evidence for inhomogeneous mixing of the gases and nonuniform composition of the layers. Work is presently under way to eliminate this difficulty.

D. Growth of GaSb and $GaAs_{1-x}Sb_x$ Alloys

A cooled-substrate holder and a range of temperature gradients in the deposition zone were explored in an effort to increase the growth rate of GaSb. The conditions used for deposition on GaAs substrates are shown in Table VI. Higher growth rates of roughly a factor of three were obtained with the steeper thermal gradients, but layers grown below 450°C were still found to be polycrystalline. This is probably related to reduced surface mobility of the reactant species at these low temperatures, and, in the future, higher temperatures will be investigated, although this is limited by the melting point of GaSb (712°C).

Since the growth rate of GaSb has been very low, it has not been possible to grow layers thick enough to be removed from the substrate for electrical measurements. In addition, as was pointed out in the last Quarterly Report, GaSb layers grown on semi-insulating GaAs

TABLE VI.

Preparation of GaSb

Sample No.	Sub. Orient.,[a] Degrees	Temperatures,[b] °C		Flow Rates,[c] cc/min		Growth Rate, Microns/hr.	Comments
		Substrate	ΔT^b	SbH_3	HCl		
3-1-68-P3	45	400	300	2.2	4.0	50	polycrystalline
12-22-67-C	0	450	175	1.1	8.0	64	polycrystalline
3-6-68-P	45	500	200	2.2	6.0	3	
3-8-68-P	45	500	200	2.2	4.0	6	H_2 carrier gas for 3000 cc/min, n-GaSb used.
3-1-68-P1	45	500	200	2.2	4.0	10	
2-29-68-P1	45	600	25	1.2	4.0	0.3	
2-29-68-P2	45	600	100	1.2	4.0	nil	

Notes:

a. Angle between substrate surface and flow direction

b. Other temperatures:
Center furnace, 750°C
Gallium furnace, 700°C
ΔT is the difference between the growth furnace temperature and the substrate temperature

c. Other flow rates, unless otherwise noted:
H_2 carrier gas for HCl, 500 cc/min
H_2 carrier gas for SbH_3, 1500 cc/min

are sufficiently strained to have degraded electrical properties. However, since these GaSb layers are p-type, deposition on n-type GaSb should provide unstrained layers electrically isolated from the substrate by virtue of the p-n junction formed at their boundary. This was attempted, but in this initial attempt, a satisfactory rectifying junction was not obtained and, therefore, this experiment will be repeated.

It has been found that smooth damage-free (100) surfaces of GaSb can be prepared by a chemical-mechanical polishing technique utilizing a 0.5% solution of bromine in methanol. This method had previously been successfully used to polish Ge,[3] Si,[3] GaAs,[4] and CdS.[5]

It has recently been predicted[6] that Gunn oscillators prepared from $GaAs_{1-x}Sb_x$ alloys with $0.2 < x < 0.6$ may exhibit lower threshold fields and higher efficiencies than devices prepared from GaAs. The broad range of compositions considered is in part due to a lack of precise knowledge of the band structure of these alloys. Several layers of these alloys have been grown, and the conditions are presented in Table VII. The highest GaSb concentration prepared to date has been only 12%; but previous workers[6] had failed, using vapor phase techniques, to incorporate more than 1% GaSb in these alloys. We see no inherent deterrent to preparing these materials, using this vapor phase method, for all values of x.

Some of these initial layers will be evaluated as Gunn oscillators.

TABLE VII

Preparation of $GaAs_{1-x}Sb_x$ Alloys

Sample No.	x	SbH_3	As	Total H_2	Growth Rate, Microns/hr.
3-4-68-P	0.005[a]	1.2	3.0	2000	4
3-12-68-P1	0.04[b]	1.2	3.0	4000	6.5
3-12-68-P2	--	2.4	1.5	4000	2.6
3-13-68-P	--[c]	2.4	3.0	4000	3.5
3-14-68-P	0.12[b]	2.4	3.0	4000	2.5

NOTES:

a. From x-ray diffraction analysis
b. From optical band gap measurement
c. Optical band gap data indicate compositional grading
d. Temperatures used:
Growth furnace, 725°C
Center furnace, 875°C
Gallium furnace,775°C

III. CONCLUSIONS AND RECOMMENDATIONS

During the first four quarters of this contract, all of the main objectives have been realized with the exception of the preparation of InSb. These include the preparation of GaAs, GaP, GaSb, InAs, InP, $GaAs_{1-x}P_x$, $GaAs_{1-x}Sb_x$, $InAs_{1-x}P_x$, $In_{1-x}Ga_xAs$, and $In_{1-x}Ga_xP$ alloys. In addition, n- and p-type doping has been achieved and multilayer structures have been prepared with selected compounds. In virtually all cases, material of very high quality has been obtained, which clearly demonstrates the versatility and general excellence of this chosen method.

During the next quarter, emphasis will be placed on preparing InSb to complete the requirements of the initial phase of this contract. In addition, the $In_{1-x}Ga_xP$ system will be studied in greater detail, and the $GaAs_{1-x}Sb_x$ system will be completed.

In accordance with the aims of the contract extension, work will be initiated for the preparation of compounds containing aluminum and nitrogen.

IV. REFERENCES

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V. NEW TECHNOLOGY APPENDIX

A. Title: Mechanical-Chemical Polishing of <100> GaSb Substrates.

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Comments: A mechanical-chemical polishing technique previously used with success on Si, Ge, GaAs, and CdS has been found to produce smooth damage-free (100) GaSb surfaces.