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INTERIM SCIENTIFIC REPORT NO. 2

PERFECTION OF MATERIALS TECHNOLOGY FOR
PRODUCING IMPROVED GUNN-EFFECT DEVICES

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Electronics Research Center
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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I. INTRODUCTION AND SUMMARY

The objective of this program is to develop improved materials for
Gunn-effect devices. Most of the effort during the past year was devoted to
investigations of the chemical vapor deposition technique for GaAs. Characteri-
zation of the materials included measurements of Hall effect and resistivity
at 300°K and at 77°K for specimens deposited on semi-insulating substrates.
The former data, together with some special measurements covering a continuous
range of temperatures, yielded information on deep-lying donor levels, while
both sets of data permitted determination of the electron mobilities. Approxi-
mately two dozen epitaxial layers of GaAs, deposited on n+ substrates placed
in the reaction tube adjacent to the semi-insulating substrates, were supplied
to ERC for device studies.

Effort was also devoted to the preparation of $Ga_xIn_{1-x}Sb$ mixed
crystals, with emphasis on the region where x ranged from 0.4 to 0.5.
Although initial efforts yielded polycrystalline material, it was found that
specimens shipped to ERC exhibited surprising low thresholds for Gunn
oscillations.

The research on vapor deposition of GaAs provided considerable
information concerning the influence of a number of preparation parameters on
the character of the deposit, including the occurrence of significant auto-
doping from Te-doped substrates. Associated with this process, appears to be
the occurrence of abnormally large ratios of carrier density at room tempera-
ture to that at 77°K, indicative either of the existence of deep-lying donor

levels or of concentration gradients. In regard to the $Ga_xIn_{1-x}Sb$, a new
technique was devised, which offers promise of providing reasonably homogeneous
crystals. Initial effort was devoted to a careful programming of the tempera-
ture gradients in the system.

II. EXPERIMENTAL DETAILS

Epitaxial GaAs--Chemical Vapor Deposition

The chemical vapor deposition of GaAs was accomplished using the
$Ga-AsCl_3-H_2$ system of reagents. The chemical reactions presumed to occur at
the Ga source and the substrate, respectively, are as follows:

$$3Ga_{(1)} + AsCl_{3(v)} \rightarrow 3GaCl_{(v)} + 1/4 \, As_{4(v)}$$

and

$$3GaCl_{(v)} + 1/2 \, As_{4(v)} \rightarrow 2GaAs_{(s)} + GaCl_{3(v)}.$$
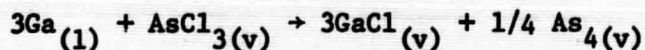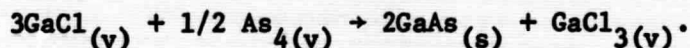
During the process of arseniding or saturating the Ga source, another
important reaction which occurs is:

$$2AsCl_{3(v)} + 3H_{2(v)} \rightarrow 6HCl_{(v)} + 1/2 \, As_{4(v)}.$$
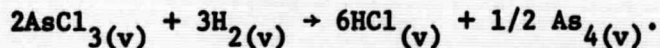
After saturation, a thin skin of GaAs forms on the surface of the
gallium. Hence, another possible reaction is:

$$GaAs_{(s)} + HCl_{(v)} \rightarrow GaCl_{(v)} + 1/4 \, As_{4(v)} + 1/2 \, H_{2(v)}.$$
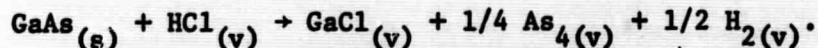
Apparatus and Materials

The reactor and furnace system employed was essentially that described in the Semiannual Technical Report No. 1, October 14, 1968. The only major modifications were: (1) the substitution of Ace teflon valves with viton "O" rings for the teflon stopcocks used previously and (2) the use of a constant temperature bath around the $AsCl_3$ bubbler to control the $AsCl_3/H_2$ ratio. This bath consisted of a two chamber jacket, a heater-controller unit, and a conventional electric water cooler. The $AsCl_3$ bubbler was placed in the inner chamber which was filled with an ethylene glycol solution. The heater-controller unit was placed in the outer chamber through which an identical ethylene glycol solution was circulated. Temperature excursions on either side of the control point were typically 4-5°C in the outer chamber, but less than 0.1°C in the inner chamber. Thus, the $AsCl_3$ temperature fluctuations could be held within 0.1°C.

All reactant materials and substrates were obtained from commercial sources. They included:

Gallium-Alusuisse	99.9999%
$AsCl_3$ - ASARCO Lot C-157	99.999+
" " C-161	"
Ohio Semitronics	99.999
Baker & Adamson	99.0
Hydrogen - Airco	99.95
Substrates - Monsanto Cr-doped	
" Te-doped	
" Si-doped.	

4

Procedure

Substrates used in this program were (1) semi-insulating Cr-doped for Hall measurements, and (2) low-resistivity Si- or Te-doped for n on n+ structures. These substrates were prepared for use by hand lapping on 4/0 silicon carbide paper and degreasing. They were then etched for 25 minutes in $5H_2SO_4$-$1H_2O_2$-$1H_2O$ rinsed in high purity (> 15×10^6 ohm-cm) deionized water, and soaked for 30 minutes in a boiling solution of the sodium salt of EDTA. The substrates were then rinsed twice in room temperature deionized water, given a final rinse in boiling deionized water, loaded onto the seed holder and inserted in the reactor under a H_2 flow of 100 cc/min. The system was then purged for approximately 2 hrs with purified H_2.

In a typical deposition procedure, the furnaces were heated up with only hydrogen flowing. When the desired temperatures were reached (800-900°C for the gallium source and 725-735°C for the deposition zone) the hydrogen was passed through the $AsCl_3$, which was held at a fixed temperature, and over the molten gallium.

The arsenic was completely absorbed by the gallium as indicated by the appearance of only gallium and $GaCl_3$ droplets on the reactor walls downstream of the furnace end. Saturation of the melt was distinctly signalled by the appearance of a continuous, blue-metallic ring on the reactor walls just at the furnace end; the time required for melt saturation was generally 2-1/2 hours for a 10-gram gallium charge. At this time the $AsCl_3$ was diverted from the Ga boat and directed to the etch tube. The substrate was inserted to a preplanned position and the deposition-furnace temperature was increased to give a substrate temperature greater than 800°C. After 10 minutes of vapor

etching _in situ_, the $AsCl_3$ was diverted over the Ga, the substrate was pulled back to the deposition position, and the deposition furnace was returned to its original temperature setting. Deposition was continued as long as desired, and was terminated by withdrawing the substrate from the furnace.

$Ga_x In_{(1-x)} Sb$--Bulk Crystal Growth

Ingots of $Ga_x In_{(1-x)} Sb$ were prepared by two techniques: the single pass zone leveling method described by Dismukes and Ekstrom[1], and a solute diffusion technique conceived by J. F. Miller of this laboratory. In the former method, chilled castings of compositions $Ga_{.11} In_{.89} Sb$ and $Ga_{.40} In_{.60} Sb$, respectively, were prepared from high purity Ga, Sb, and InSb. A one-inch long section of the $Ga_{.11} In_{.89} Sb$ and a 6-inch long section of the $Ga_{.40} In_{.60} Sb$ castings were placed end to end in a silica boat and inserted into a silica reaction tube. A single pass was made with a 1-inch molten zone at a travel rate of 0.12 inch per hour. The direction of zone travel was such that the $Ga_{.11} In_{.89} Sb$ section was the first to melt. The complete pass took 72 hours.

In the solute diffusion method, an indium-gallium alloy of the desired composition, say, $In_{0.6}-Ga_{0.4}$, along with a quantity of antimony, contained in a sealed silica tube of the type shown in Fig. 1 is placed in a furnace in a temperature profile such as is indicated in the figure. In such a profile, antimony will slowly distill or sublime and will enter the indium-gallium solution by vapor transport at a rate that can be controlled by controlling the antimony temperature, T_c. If the transport rate is sufficiently low,

(1) J. P. Dismukes and L. Ekstrom, Trans. Met. Soc. AIME __223__, 672 (1965).
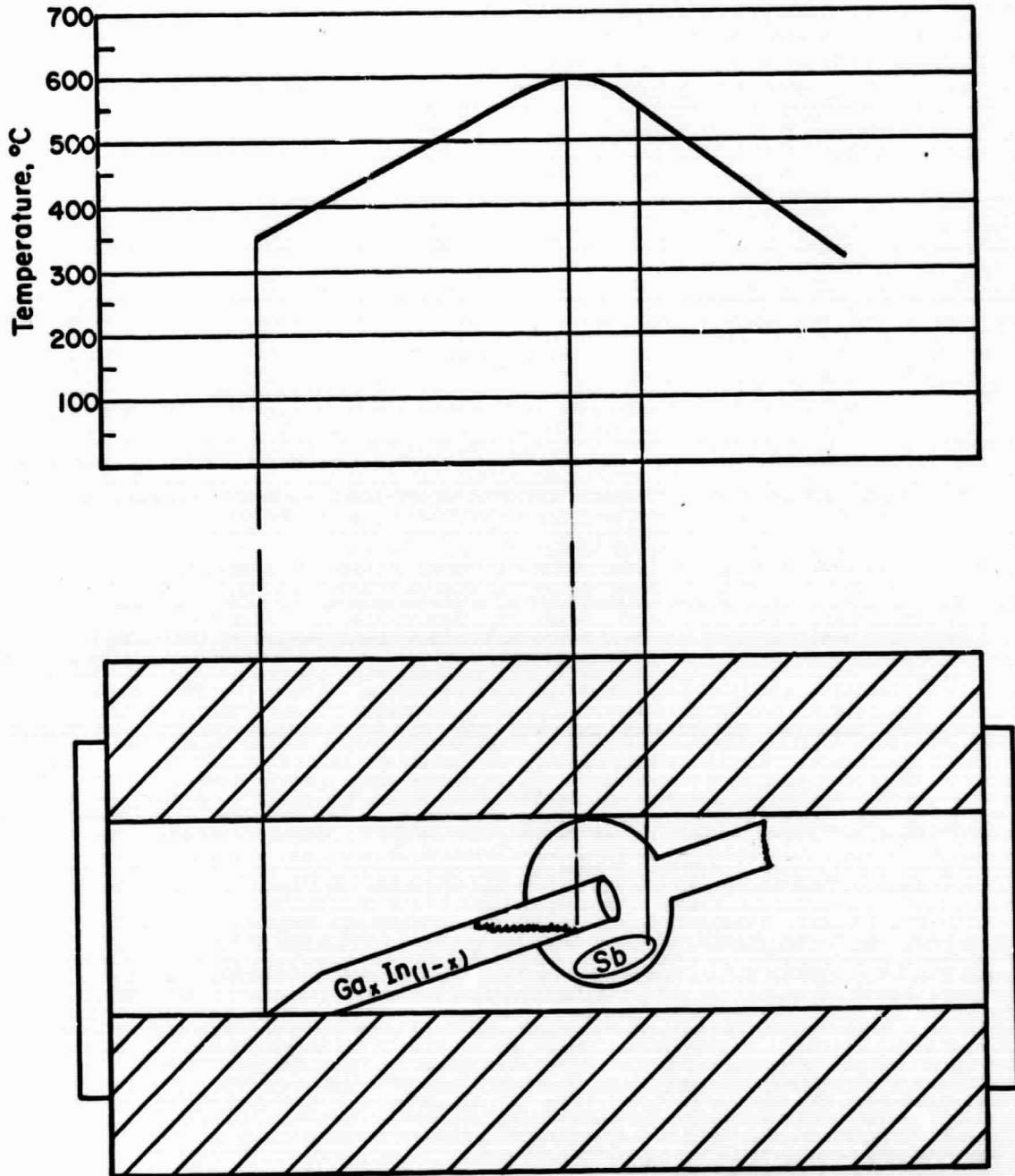
FIGURE 1. APPARATUS AND TEMPERATURE PROFILE FOR CRYSTAL GROWTH
BY SOLUTE DIFFUSION

when the concentration of antimony in the In_x-Ga_{1-x} solution has reached the concentration corresponding to saturation at the lowest solution temperature, T_L, $In_xGa_{1-x}Sb$ will continue to form at the lowest-temperature site in the solution until all of the antimony has sublimed.

Four rates are of concern in the overall process:

r_1 - the rate of transport of antimony vapor to the In-Ga solution,

r_2 - the rate of solution of antimony in the In-Ga at the liquid surface,

r_3 - the rate of diffusion of antimony through the In-Ga solution,

r_4 - the rate of crystallization of $In_xGa_{1-x}Sb$ at the low-temperature site.

If r_1 is kept low so that $r_1 < r_2 = r_3 = r_4$, saturation of the In-Ga solution will never be catastrophically exceeded, and the composition of crystallizing $In_xGa_{1-x}Sb$ (equilibrium) solid will remain constant (corresponding to the initial In_x-Ga_{1-x} composition) and the alloy will be of uniform composition. The rate of deposition alone will change as the solid-liquid interface moves into the higher temperature region.

Since no temperature or mechanical-movement program is involved, minimum difficulty should be encountered in maintaining a steady-state process and avoiding solvent inclusions. With modified experimental procedure, seeding of growth is possible.

Electrical Measurements

Specimens of epitaxial GaAs and bulk $Ga_xIn_{1-x}Sb$ prepared under the present contract were characterized by Hall coefficient and resistivity measurements. Data for the epitaxial GaAs samples were obtained via the Van der Pauw technique from samples for which the epitaxial layers were grown on Cr-doped semi-insulating GaAs substrates. Data for the bulk $Ga_xIn_{1-x}Sb$ specimens were obtained on rectangular parallelepipeds. In all cases a magnetic field of 8770 gauss was used for the Hall effect measurements. Conventional d.c. potentiometric techniques were employed, using a constant current source in conjunction with either a Leeds and Northrup K-3 potentiometer or, for high resistance samples, a Keithley model 610 electrometer. Measurements were made routinely at 300 and 77°K. In addition, measurements as a function of temperature were obtained on selected samples of GaAs in order to check for the presence of deep levels,and on selected samples of $Ga_xIn_{1-x}Sb$ in order to determine the band gap and from that, the alloy composition.

III. EXPERIMENTAL RESULTS

Epitaxial GaAs

The pertinent electrical properties of GaAs epitaxial layers prepared by the $Ga/AsCl_3$ reagent system were found to depend not only on overall system cleanliness and purity of reagents, but also on the unused fraction of $AsCl_3$ remaining in the bubbler (bubbler fraction),the mole fraction

of $AsCl_3$ present in the flow stream, and the temperature of the Ga source.
In addition, when layers were deposited onto low resistivity and semi-
insulating substrates simultaneously, the relative locations of the two types
of substrates on the reactor and the particular dopant in the low resistivity
substrate influenced the purity and uniformity of the epitaxial layers.

The effects of bubbler fraction and $AsCl_3$ source on the purity of
GaAs layers are demonstrated in Figure 2, which shows carrier concentration versus
bubbler fraction for $AsCl_3$ charges obtained from various sources. In each
case the initial charge of $AsCl_3$ was 50 gm, the Ga source temperature was 850°C,
and the $AsCl_3$ bubbler was at room temperature, corresponding to an $AsCl_3/H_2$
ratio of approximately 1 mole percent. In the case of Asarco Lot C-157
$AsCl_3$, the carrier concentration was initially on the order of $10^{17} cm^{-3}$,
but decreased monotonically with decreasing bubbler fraction, the resulting
layers becoming p-type after 30-35% of the total charge had been exhausted.
The Baker and Adamson reagent grade $AsCl_3$ behaved in a totally different
manner, however. In this case the carrier concentration increased gradually
from an initial value of $4.4 \times 10^{15} cm^{-3}$ with decreasing bubbler fraction.
Since the pertinent deposition parameters were the same for all the data
presented in Figure 2, it appears that the difference between the Baker and
Adamson and the Asarco charges may be attributed to variations in the
concentration and species of impurities in the $AsCl_3$. That is, it appears
that in the Asarco $AsCl_3$, donor impurities are present primarily in a highly
volatile form. With successive depositions, corresponding to decreasing bubbler
fraction, the concentration of these donors is depleted until it is less than
the concentration of background acceptors, at which point p-type layers result.
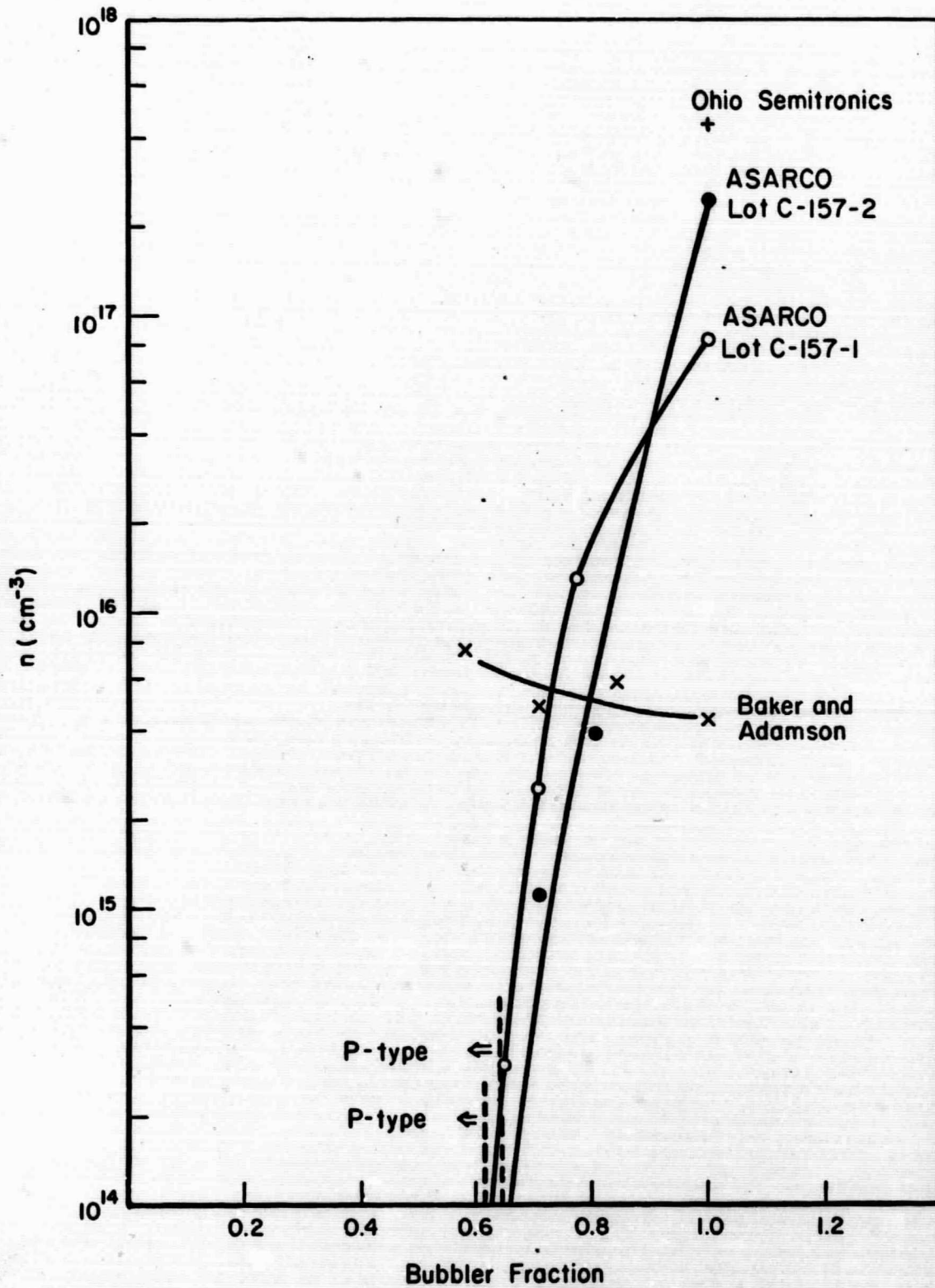
FIGURE 2. VARIATION OF CARRIER CONCENTRATION WITH BUBBLER FRACTION
FOR VARIOUS AsCl₃ SOURCES

Conversely, in the case of Baker and Adamson $AsCl_3$, the donors are primarily present in the form of a relatively nonvolatile species, so that their concentration increases with decreasing bubbler fraction.

The inability to obtain device quality material from apparently pure $AsCl_3$ with the deposition conditions described in connection with Figure 2 led to a series of experiments on the effects of gallium source temperature and $AsCl_3/H_2$ ratio on the electrical properties of epitaxial layers. The results of these experiments appear in Tables I and II.

The depositions listed in Table I were obtained with the remaining two thirds of a 50 gm charge of Asarco Lot C-157 $AsCl_3$. The deposition just prior to the first entry in Table I, was made under the conditions of Figure 2 (T_{Ga} = 850°C, $AsCl_3/H_2 \geq 1$ mole %), and was p-type. Upon increasing the gallium source temperature to 900°C and decreasing the bubbler temperature to 5°C, the n-type layer 26645-44-25 resulted. Continued operation with T_{Ga} = 900°C and $AsCl_3/H_2 \leq 0.64\%$ yielded n-type layers with acceptable values of carrier concentration and electron mobility at a bubbler fraction as low as 0.42 (deposition 73-25). Upon decreasing T_{Ga} to 800°C with $AsCl_3/H_2$ = 0.64, the p-type sample 75-31 resulted. A subsequent decrease of $AsCl_3/H_2$ to 0.44% while maintaining T_{Ga} at 800°C again resulted in an n-type layer (80-26).

Analogous results were obtained with fresh 50 gm charges of Asarco Lot C-161 $AsCl_3$ as shown in Table II. In this case, however, initial saturation of the Ga source occurred at 800°C. Seven consecutive depositions (26645-83-3 to 97-25) were made with T_{Ga} = 800°C, the first four at an $AsCl_3/H_2$ ratio of 0.64 mole percent and last three at an $AsCl_3/H_2$ ratio of 0.77 mole percent. Increasing T_{Ga} to 900°C, resulted in electron concentrations of 3.53×10^{16} and

TABLE I. EFFECT OF GROWTH CONDITIONS ON GaAs
LAYERS PREPARED FROM ASARCO LOT C-157
$AsCl_3$

Deposition	T_{Ga} (°C)	$AsCl/H_2$ (mole %)	$n(cm^{-3})$		$\mu(cm^2/v\text{-}sec)$		Bubbler Fraction
			300°K	77°K	300°K	77°K	
26645-44-25	900	0.45	7.77×10^{15}	5.39×10^{15}	4880	23,200	0.68
46-27	900	0.47	4.18×10^{15}	3.07×10^{15}	5330	31,800	0.66
48-26	900	0.49	5.30×10^{15}	3.81×10^{15}	5320	30,200	0.64
50-26	900	0.53	1.66×10^{15}	1.38×10^{15}	6240	47,700	0.61
65-26	900	0.64	2.03×10^{15}	1.45×10^{15}	4790	36,300	0.52
69-27	900	0.64	1.95×10^{15}	1.44×10^{15}	5020	41,300	0.48
73-25	900	0.64	5.34×10^{15}	3.51×10^{15}	4050	23,600	0.42
75-31	800	0.64	p-type				0.40
80-26	800	0.44	2.08×10^{15}	1.86×10^{15}	5630	30,300	0.39

TABLE II. EFFECT OF GROWTH CONDITIONS ON GaAs LAYERS
PREPARED FROM ASARCO LOT C-161 AsCl$_3$

Deposition	T_{Ga} (°C)	AsCl/H$_2$ (mole %)	n(cm^{-3})		μ(cm^2/v-sec)		Bubbler Fraction
			300°K	77°K	300°K	77°K	
26645-83-3	800	0.64	6.73×10^{15}	5.04×10^{15}	5170	23,700	1
85-26	800	0.64	4.63×10^{15}	3.10×10^{15}	4220	23,200	0.97
89-26	800	0.64	4.78×10^{15}	3.26×10^{15}	4740	27,100	0.94
91-26	800	0.64	5.21×10^{15}	3.61×10^{15}	5060	34,200	0.92
93-25	800	0.77	5.63×10^{15}	4.19×10^{15}	5500	31,900	0.90
95-25	800	0.77	1.81×10^{15}	1.62×10^{15}	6380	50,900	0.89
97-25	800	0.77	2.62×10^{15}		4900		0.87
99-26	900	0.77	3.53×10^{16}		3680		0.84
26681-5-25	900	1.5	1.48×10^{16}		4340		0.80
7-28	823	1.05	High resistivity				0.79
9-26	823	0.77	High resistivity				0.77
16-25	850	0.77	2.41×10^{16}		3700		0.64
33-1	810	p-type					0.55
37-25	850		1.39×10^{16}		4760		0.52
39-25	850		1.04×10^{16}		3400		0.50
41-28	840	0.77	8.70×10^{15}		4220		0.48
43-26	825	0.77	1.19×10^{15}	1.00×10^{15}	6100	44,700	0.47
45-27	825	0.77	1.21×10^{15}	1.01×10^{15}	6280	48,800	0.45
49-26	825	0.77	6.67×10^{14}	7.31×10^{14}	7000	52,100	0.42
53-26	825	0.77	p-type				0.39
55-26	825	0.56	5.68×10^{14}	5.84×10^{14}	3450	21,100	0.35

1.48×10^{16} at $AsCl_3/H_2$ ratios of 0.77 and 1.5%, respectively (depositions 99-26 and 26681-5-25). During the series of depositions yielding layers 26681-7-28 through 39-25, the Ga temperature was cycled to yield high and low resistivity n-type layers, and to change the conductivity type from n to p and back to n. Depositions 39-25 through 55-26 reveal, respectively, the following behavior: (a) the reduction in carrier concentration achieved by programming the gallium temperature from 850 to 825°C with the $AsCl_3/H_2$ ratio fixed at 0.77 percent (39-25 through 43-26); (b) the conversion to p-type at a bubbler fraction of 0.39 (deposition 53-26); and (c) the conversion back to n-type by lowering the $AsCl_3/H_2$ ratio from 0.77 to 0.56 percent (deposition 55-26).

Based on the effects of T_{Ga} and $AsCl_3/H_2$ ratio in film properties as evidenced by the data in Table II, growth conditions were chosen to yield device quality layers and applied to the series of depositions presented in Table III. The results presented in Table III indicate that by appropriate initial choice and suitable adjustment of growth parameters, a high yield of device quality material can be obtained.

In addition to the effects of reagent purity and deposition parameters, an auto-doping of layers was observed when Te or Si doped low resistivity substrates were employed. In the case of Si-doped substrates this effect was only noticeable for samples located downstream from the doped substrate. For example, depositions 68-26 T,B, and 70-27 F,R, employed 4 substrates, 2 each of the semi-insulating and Si-doped variety. In the case of deposition 68-26, layers were grown simultaneously on four substrates so arranged that one set of two substrates (1 Cr-doped + 1 Si-doped) was located immediately above the

TABLE III. ELECTRICAL PROPERTIES OF GaAs EPITAXIAL LAYERS

Deposition	T_{Ga} (°C)	$AsCl/H_2$ (mole %)	$n(cm^{-3})$		$\mu(cm^2/v\text{-}sec)$		Bubbler Fraction
			300°K	77°K	300°K	77°K	
26681-60-27	810	0.77	4.01×10^{15}	3.31×10^{15}	6120	30,500	1
62-27	810	0.77	1.14×10^{15}	9.25×10^{14}	5700	45,700	0.98
64-27	810	0.77	3.36×10^{15}	2.12×10^{15}	5140	52,300	0.97
66-26	800	0.77	High resistivity				0.93
68-26T	825	0.77	2.68×10^{14}	3.93×10^{14}	6630	42,900	0.76
68-26B			3.14×10^{14}	3.57×10^{14}	5530	37,400	
70-27F	825	0.77	9.23×10^{13}	1.70×10^{14}	5350	35,600	0.74
78-27R	825	0.77	2.67×10^{15}	1.84×10^{18}	4850	36,200	
73-3	825	0.76	1.63×10^{14}	2.37×10^{14}	6560	60,400	0.73
75-28	825	0.57	4.08×10^{15}	2.92×10^{15}	5130	40,200	0.71
77-27	825	0.65	8.11×10^{14}	8.20×10^{14}	5150	41,400	0.68
81-26	825	0.57	1.38×10^{15}	1.21×10^{15}	5530	51,300	0.65
86-25	825	0.57	4.46×10^{14}	4.73×10^{14}	5470	45,700	0.61

second set. Thus all four substrates were in the same portion of the furnace profile. The data of Table III indicate that little autodoping from the Si-doped substrate occurred. In the case of deposition 70-27, one set of substrates was located upstream from the other. In this case, doping of the layer is evident for the downstream substrate 70-27R.

When Te-doped substrates were employed, significant auto doping occurred irrespective of the relative positions of the Te- and Cr-doped substrates. Measured carrier concentrations of 1-2 x 10^{16} cm^{-3} were invariably observed when Te-doped substrates were present in the reactor. In addition, whenever auto-doping was known to occur from either Si- or Te-doped substrates, the resulting layers exhibited an anomalous temperature dependence of the Hall coefficient R_H. These effects are summarized in Table IV.

Examination of the data in Table IV indicates that Te auto doping occurred during depositions 52-27 and 54-28 and that Si auto doping occurred during depositions 47-26 and 51-26. It may also be observed that the room temperature mobility is anomalously low and the ratio $R_H 77/R_H 300$ is anomalously high for the auto-doped samples. It is possible that the reduction in room temperature mobility and the increase in apparent freezeout at low temperatures is due to the presence of a deeper-lying level associated with the normally hydrogenic Si and Te donors, e.g., an impurity complex of Si or Te with lattice defects, oxygen, Ga or As. However, since Te doping during vapor deposition has been successfully employed elsewhere to produce device quality GaAs, it seems more likely that the observed effects result from an inhomogeneous distribution

TABLE IV. EFFECT OF SUBSTRATE DOPANT ON GaAs LAYERS

Deposition	Substrate Dopant	AsCl$_3$	R_H cm^3/coul	ρ ohm-cm	μ cm^2/v-sec	T°K	$R_H 77/R_H 300$
26645-50-26	--	Asarco C-157	-3770	0.604	6,240	300	1.20
			-4520	0.0948	47,700	77	
52-27[1]	Te	"	- 426	0.135	3,170	300	1.80
			- 767	0.0597	12,800	77	
54-28[1]	Te	"	- 331	0.125	2,650	300	1.85
			- 613	0.0574	10,700	77	
65-26	--	"	-3080	0.643	4,790	300	1.40
			-4320	0.119	36,300	77	
26881-43-26	--	Asarco C-161	-5250	0.859	6,100	300	1.18
			-6220	0.319	44,200	77	
45-27[2]	Si		-5150	0.820	6,280	300	1.20
			-6200	0.127	48,800	77	
47-26[3]	Si		-1090	0.266	4,100	300	2.18
			-2380	0.0545	43,700	77	
49-26[2]	Si		-9370	1.34	7,000	300	0.91
			-8550	0.164	52,100	77	
51-26[3]	Si		-1980	0.432	4,600	300	1.65
			-3270	0.0883	37,000	77	

(1) Te and Cr doped substrates side by side

(2) Si and Cr doped substrates side by side

(3) Si doped substrate upstream.

of the dopant in the auto-doped layers. Reid et al.[2] employed Schottky

capacitance measurements to investigate Te auto doping and verified the existence

of nonuniform donor distributions in the auto doped layers.

$$\text{Bulk } Ga_x In_{1-x} Sb$$

Zone Leveling

As discussed previously, two methods were employed to produce bulk

ingots of $Ga_x In_{1-x} Sb$. Since the solute diffusion method is still in the

exploratory stage, only the single pass method described by Dismukes and

Ekstrom[1] was responsible for the samples suitable for electrical characteriza-

tion. The room temperature electrical properties of selected samples taken

from various portions of an ingot prepared by the single pass method are listed

in Table V.

TABLE V. VARIATION OF ELECTRICAL PROPERTIES OF
$Ga_x In_{1-x} Sb$ WITH ALLOY COMPOSITION

Sample	R_H $cm^3/coul$	ρ ohm-cm	$\|R_H/\rho\|$ $cm^2/v\text{-}sec$	$\|1/R_H e\|$ cm^3	Alloy Composition
A	− 628	0.0117	53,700	9.95×10^{15}	$Ga_{.15}In_{.85}Sb$
B	−1790	0.144	12,400	3.49×10^{15}	$Ga_{.41}In_{.59}Sb$
C	−3460	0.413	8,400	1.80×10^{15}	$Ga_{.49}In_{.51}Sb$
D	+ 610	1.52	400	1.02×10^{16}	$Ga_{.68}In_{.32}Sb$

(2) F. J. Reid and L. B. Robinson, in "Gallium Arsenide" (Proc. 2nd Intern.
Symposium, Dallas, Texas, 1968), p. 59. Inst. Phys. and Phys. Soc.,
London, 1969.

Alloy compositions were determined by x-ray emission spectroscopy.
For Samples A and C, detailed measurements of the electrical properties were
obtained as a function of temperature as shown in Figures 3 and 4. These data
in the intrinsic region were used to estimate the $0°K$ energy gap E_g. The
resulting values of E_g were then compared with the data of Woolley and Gillette[3]
to obtain an independent estimate of alloy composition. The agreement between
these values and those obtained by x-ray emission were within the accuracy
($\pm$ 5%) of the latter method.

For large In content as in Sample A, Table V and Fig. 3, material was
n-type at both 77 and $300°K$, and intrinsic conduction dominated at room tempera-
ture. For larger Ga contents (slices B and C Table V and Figure 4), the samples
were p-type in the extrinsic region, the Hall coefficient changing sign between
77 and $300°K$. In this respect the alloy composition $Ga_{.68}In_{.32}Sb$ resembled undoped
GaSb.

Additional x-ray emission studies on slices taken from that portion
of the ingot defined by Slices B and C indicated that a region of uniform
composition ($Ga_{.41}In_{.59}Sb$) extended over the center third of the ingot. Composi-
tion profiles, obtained by x-ray emission, indicated that the slices were at
least macroscopically uniform.

Solute Diffusion

In perfecting a new crystal growth technique, it is necessary to
determine optimum values of temperature and temperature gradients in the
critical regions (see Fig. 1). Initial investigations were made with tempera-
tures, T_H, in the hot zone of 550 and $600°C$. The temperature gradient in the growth

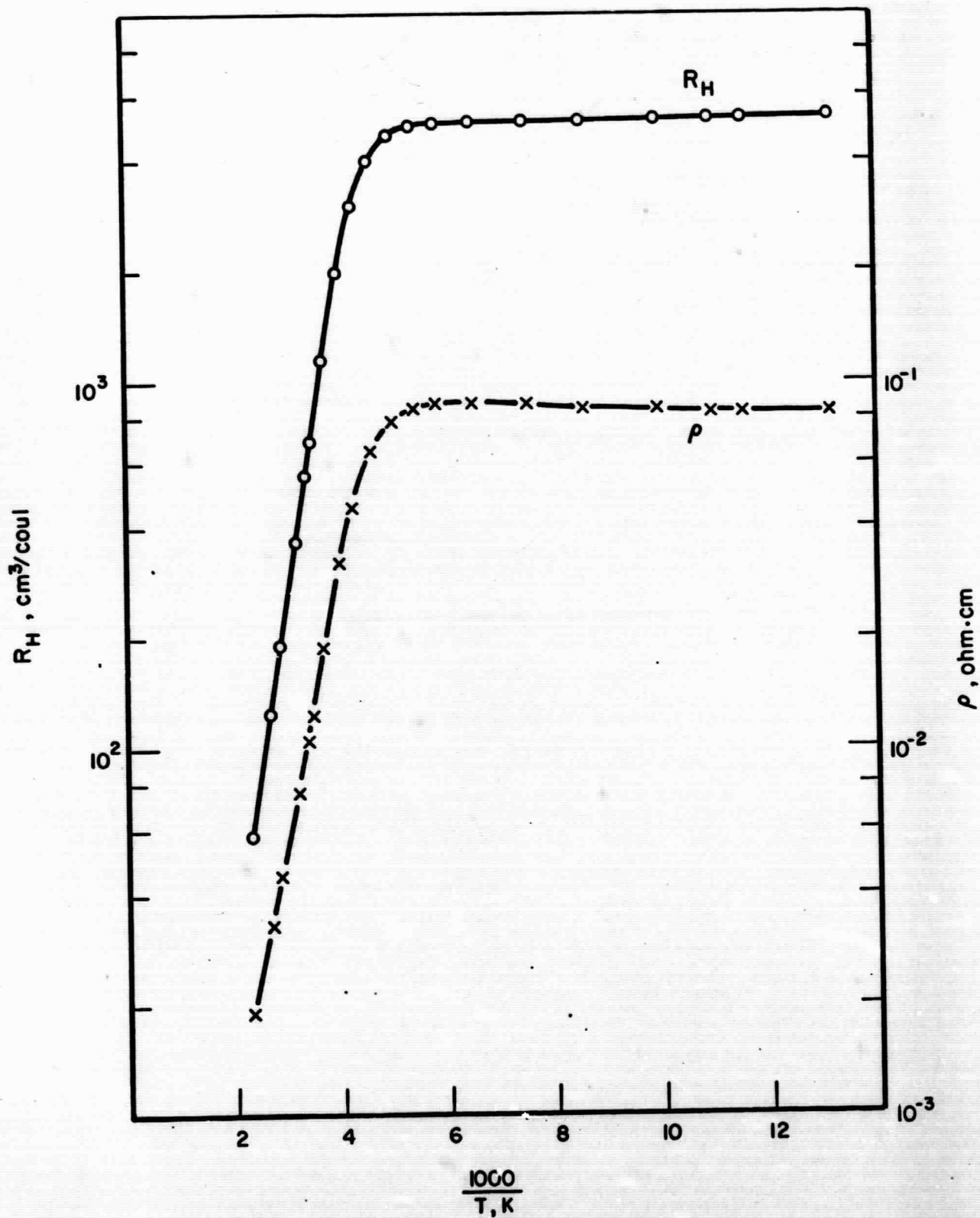(3) J. C. Woolley and C. M. Gillette, J. Phys. Chem. Solids 17, 34 (1960).

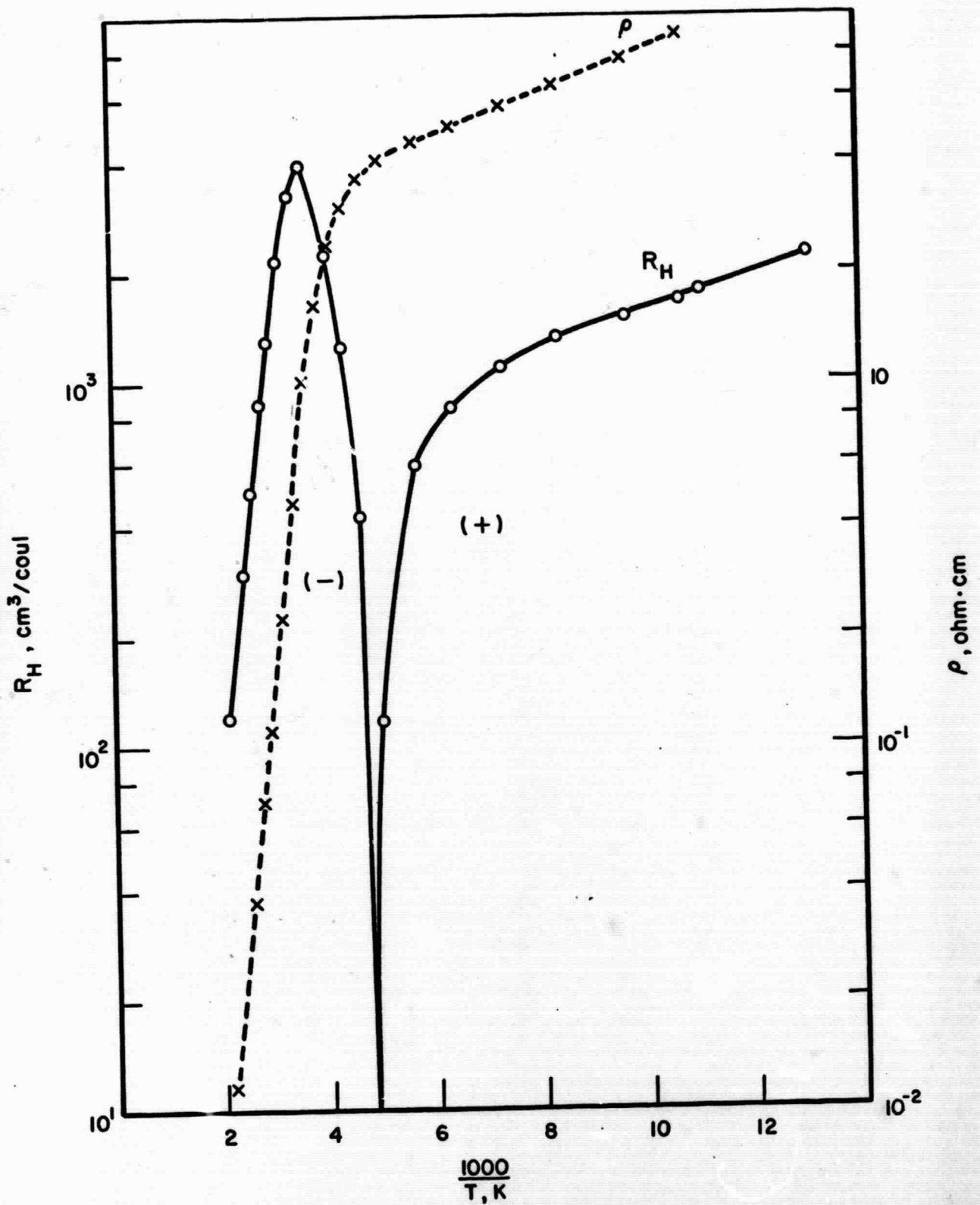FIGURE 3. TEMPERATURE DEPENDENCE OF HALL COEFFICIENT AND RESISTIVITY FOR $Ga_{.15} In_{.85}Sb$

FIGURE 4. TEMPERATURE DEPENDENCE OF HALL COEFFICIENT AND RESISTIVITY FOR $Ga_{.49}In_{.51}Sb$

zone was approximately 30°C per inch, and a melt composition $In_{0.6}Ga_{0.4}$ was employed. Under these conditions, it was found that the antimony vapor pressure was too low to form a coherent ingot in a period as long as three weeks. By raising T_H to 750°C, a solid ingot was formed in approximately four days. The ingot, however, was polycrystalline and contained solvent (Ga-In) inclusions. Inasmuch as the inclusions were large in the first-to-form portion of the ingot, it appears that the rate of transport of antimony had been too high in the initial portion of the run. Presence of small metal inclusions in the last-to-form portion of the ingot is believed to be indicative of constitutional supercooling.

A growth run with T_H at 650°C was successful in decreasing the size and density of inclusions but not in their complete elimination. Clearly, further refinements of this crystal growth technique are required. The results to date have been encouraging, however, and it is felt that through modification of conditions to permit greater flexibility of control over T_H, and to permit programming of this parameter from an initial low value to a selected steady-state value, the technique will yield improved crystals.

IV. CONCLUSIONS AND RECOMMENDATIONS

The results obtained in the chemical vapor deposition of GaAs with the $Ga/AsCl_3$ reagent scheme demonstrate the importance of adequate control of both the Ga source temperature and the $AsCl_3/H_2$ ratio in obtaining high mobility, low carrier concentration GaAs. The variations achieved in both carrier concentration and conductivity type suggest that by programming the Ga or $AsCl_3$ bubbler temperatures during growth, it may be feasible to produce layers with controlled concentration gradients or p-n junctions without the use of an

external source of dopants. The mechanisms responsible for the observed effects are not clearly understood, however. This suggests that although a number of laboratories are successfully producing high quality GaAs for device applications, a fundamental investigation of the $Ga/AsCl_3$ system of vapor growth is needed, especially as regards the thermodynamics and kinetics of the process.

The results obtained with $Ga_x In_{1-x} Sb$ alloys are encouraging from several standpoints. The fact that bulk specimens of the alloy showed microwave oscillations at reduced threshold voltage[4] in spite of their lack of crystalline perfection and uniformity establishes this material as a prime candidate for Gunn-type oscillators. If the development of the solute diffusion method of crystal growth initiated during this contract affords the opportunity to produce $Ga_x In_{1-x} Sb$ specimens of superior perfection and homogeneity, then it should be possible to ascertain the true device potential of the alloy system. In addition, the preparation technique may have application in other hard-to-prepare alloy systems. It is therefore recommended that development of the solute diffusion technique of crystal growth be actively pursued, particularly with respect to the preparation of $Ga_x In_{1-x} Sb$.

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(4) W. D. Straub, private communication.