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DEVELOPMENT OF GALLIUM ARSENIDE FOR INFRARED WINDOWS.(U)
SEP 76 H C HAFNER, M J BRAU F33615-75-C-5274
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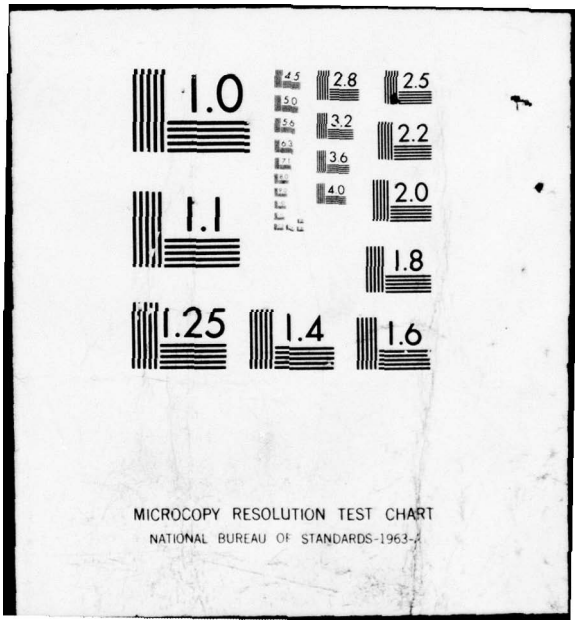
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DEVELOPMENT OF GALLIUM ARSENIDE FOR INFRARED WINDOWS

TEXAS INSTRUMENTS INCORPORATED
P. O. BOX 6015
DALLAS, TEXAS 75222

SEPTEMBER 1976

FINAL REPORT FOR PERIOD 25 JUNE 1975 - 25 JUNE 1976

Approved for public release; distribution unlimited

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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David W. Fischer
Project Engineer/Scientist

FOR THE COMMANDER

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: AFML-TR-76-163	2. GOVT ACCESSION NO.: 678300
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE *(and Subtitle)*: DEVELOPMENT OF GALLIUM ARSENIDE FOR INFRARED WINDOWS	5. TYPE OF REPORT & PERIOD COVERED: Final Report, 25 June 1975 – 25 June 1976
6. PERFORMING ORG. REPORT NUMBER:	
7. AUTHOR(s): Harold C. Hafner, Maurice J. Brau	8. CONTRACT OR GRANT NUMBER(s): AF33615-75-C-5274
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Texas Instruments Incorporated, Equipment Group, P.O. Box 6015, Dallas, Texas 75222	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Project 7371, Task 737101, Work Unit 73710144; 62102F
11. CONTROLLING OFFICE NAME AND ADDRESS: Air Force Materials Laboratory (AFML/LPO), Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433	12. REPORT DATE: September 1976 13. NUMBER OF PAGES: 48
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*: DCASO-Texas Instruments Incorporated, P.O. Box 6015 M/S 256, Dallas, Texas 75222	15. SECURITY CLASS. *(of this report)*: UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

infrared
IR window
gallium arsenide

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A program was initiated to scale-up from 6 by 4 by 0.5 inch to 6 by 12 by 0.5 inch, a GaAs gradient-freeze process for producing gallium arsenide infrared windows.

A process was developed that permits the production of gallium arsenide at atmospheric pressure, using a helium vent system. GaAs plates up to 6 by 12 by 0.4 inch were produced by this technique. The atmospheric process also permits further scale-up because ampuls can be easily fabricated and do not require special sizes, shapes and thicknesses.

The dn/dt of gallium arsenide was measured and reported. The transmittance of the plates produced was measured and reported.

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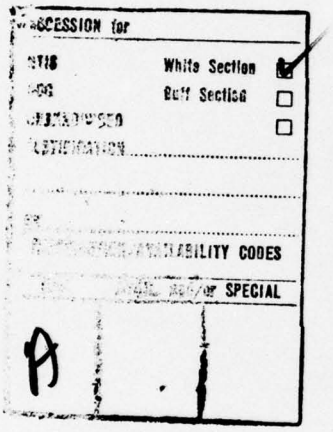
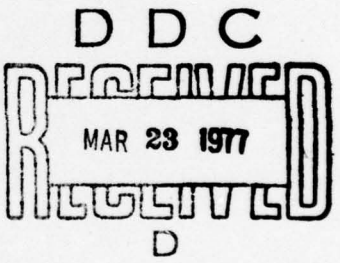
PREFACE

This report was prepared by Texas Instruments Incorporated, Dallas, Texas, under Contract F33615-75-C-5274, Project 7371, Task 737101. The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Mr. David W. Fischer (AFML/LPO) was project engineer. The work at Texas Instruments was performed in the Infrared Materials Branch of the Advanced Technology Department, which is part of the Electro-Optics Division of the Equipment Group. The project manager was Mr. Maurice J. Brau. Mr. Harold C. Hafner was project engineer and was assisted by Mr. Kenneth Johnson. The final technical report covers work conducted from June 25, 1975 to June 25, 1976. This report was submitted by the authors July 1976.





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A. GENERAL

FLIR sensors are currently being developed for high performance aircraft such as the F-4, F-111 and B-1. Application of these sensors at high speed requires a window material that exhibits little optical degradation at elevated temperatures, transmits infrared radiation in the 8- to 12-μm wavelength range with little or no loss due to absorption, and possesses a high degree of rain erosion resistance.

Development efforts for the 10.6-μm high-energy laser window suggested that the properties of gallium arsenide were desirable for a high-speed reconnaissance window. Its absorption coefficient was found to be too high for the 10.6-μm high-energy laser applications, but its performance capability as a passive infrared component at elevated temperatures was shown to be superior to germanium in the 8- to 12-μm wavelength region.

The goals of this program were: to demonstrate fabrication techniques capable of producing 6- by 12- by ½-inch thick polycrystalline gallium arsenide windows and to design and fabricate ampuls capable of producing 12- by 18- by 3/4-inch thick gallium arsenide window blanks.

B. BACKGROUND FOR SCALE-UP STUDIES

Work performed previously at Texas Instruments Incorporated under Contract F33615-75-C-1066[1] has shown the feasibility of producing excellent quality gallium arsenide plates in sizes up to 4- by 6- by 0.5-inches. This material had nearly theoretical transmittance over the 2- to 12-μm wavelength region at temperatures up to 200°C. Figures 1 and 2 show the transmittance of typical high resistivity gallium arsenide windows at 200°C. These near intrinsic properties were achieved by compensating excess shallow donors with the deep level acceptor chromium. In addition, gallium oxide was added to the melt to reduce the concentration of electrically active impurities, particularly silicon. A detailed treatise of this compensation mechanism was discussed in a previous report.[1]

[1] AFML-TR-75-49 "Development of Gallium Arsenide for Infrared Windows."

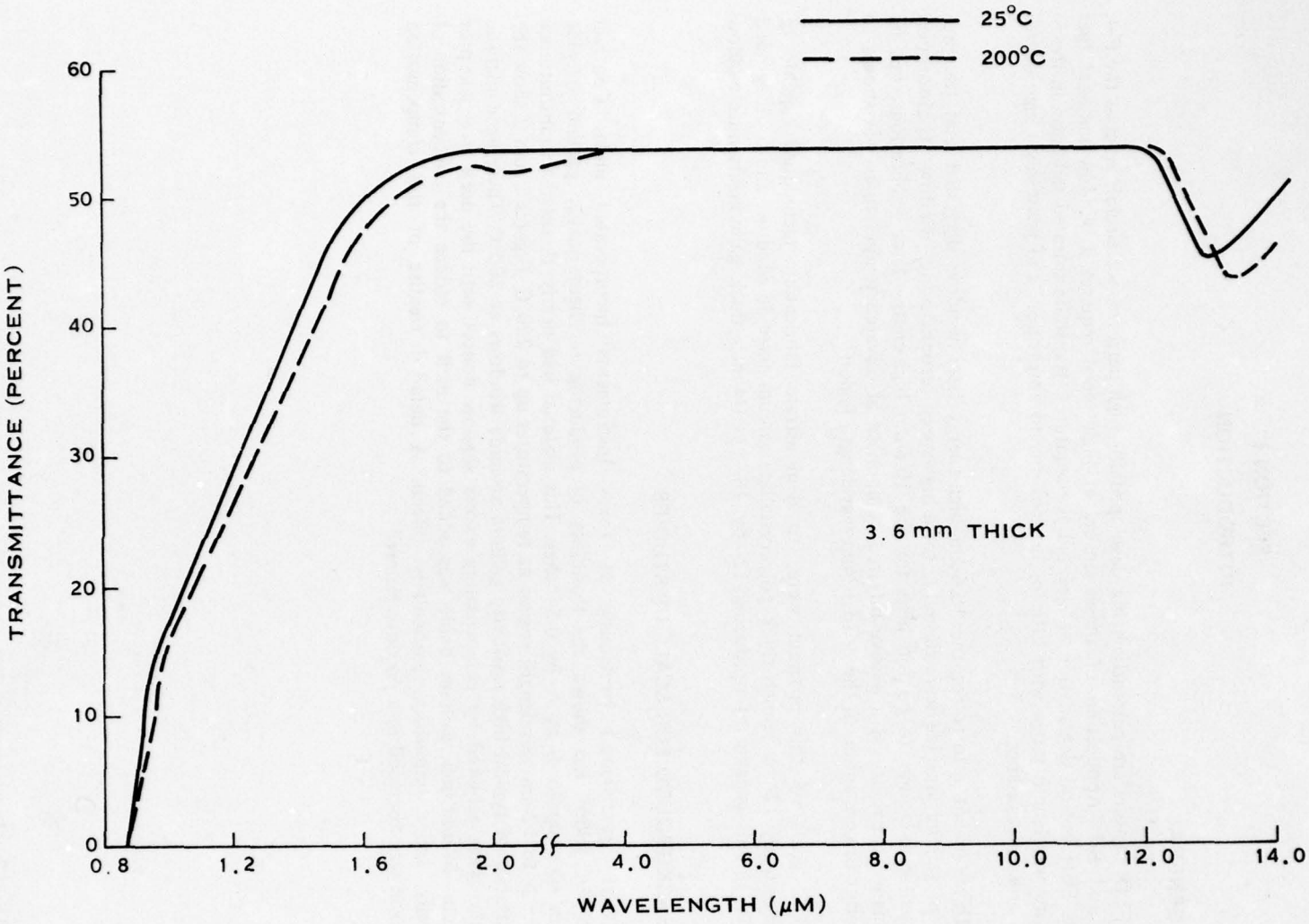

Figure 1. Transmittance Versus Temperature for 0.5 ppm Chromium-Doped Gallium Arsenide

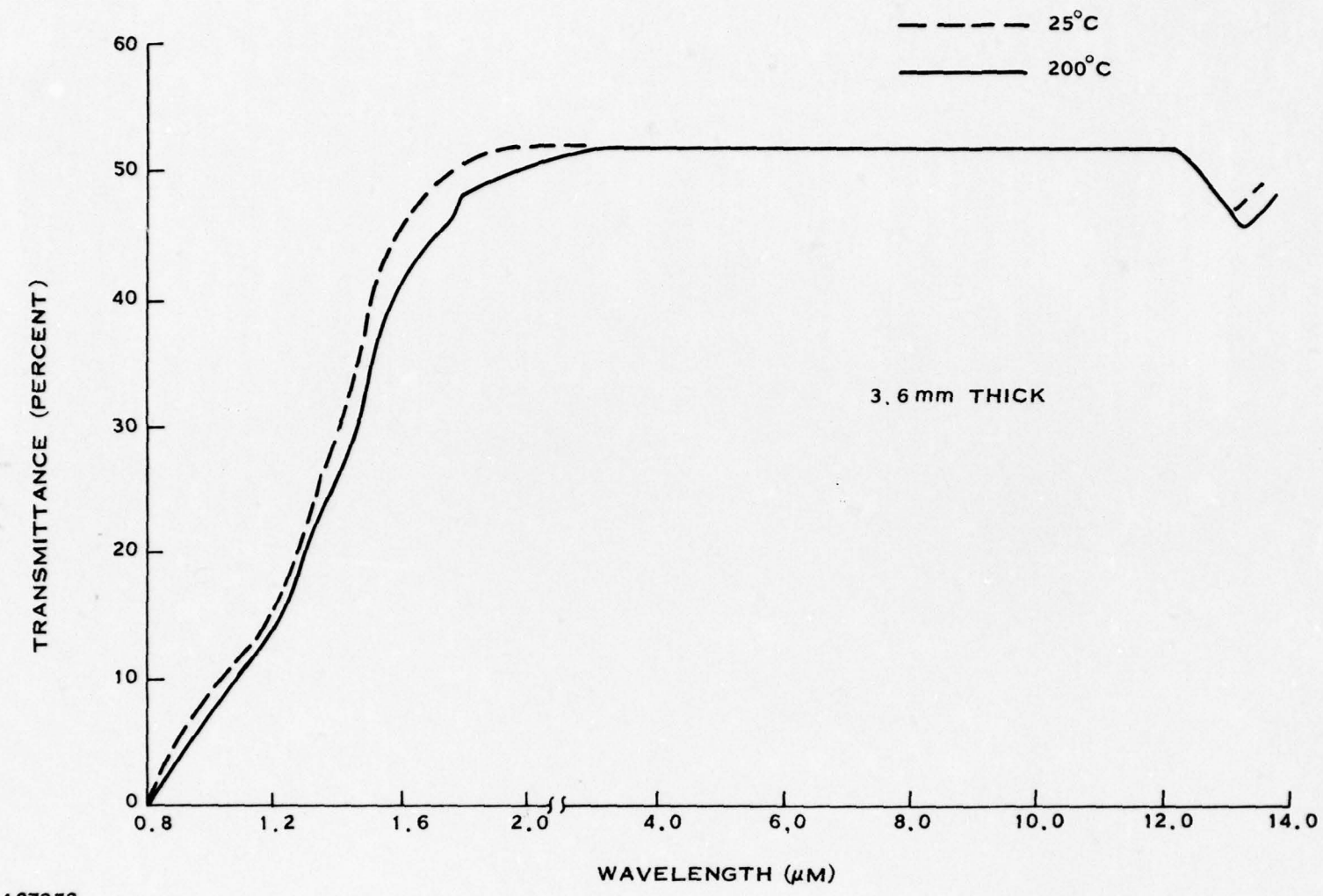

Figure 2. Transmittance Versus Temperature for 1.0 ppm Chromium-Doped Gallium Arsenide

SECTION II
GALLIUM ARSENIDE PREPARATION

A. GENERAL

The most practical technique for preparing large plates of gallium arsenide is a horizontal gradient-freeze technique. This is due to the relatively high melting point (1238°C), high arsenic vapor pressure at the melting point (approximately 0.9 atmosphere) and the tendency for gallium arsenide to expand upon freezing. In this method, the melt is contained in a suitable quartz boat inside a quartz ampul. A thermal gradient approximately 1°C per inch is established down the length of the melt. The minimum compounding temperature is at least 1240°C. The arsenic pressure is controlled by a second furnace held at 610° to 620°C. As the overall temperature of the melt is lowered, the temperature gradient passes through the melt. This results in a slow directional freeze, the rate of growth being controlled by the rate of temperature decrease.

B. PREPARATION AND GROWTH OF GALLIUM ARSENIDE

The gradient freeze process was chosen for development to produce large plates for windows since it could be adapted to prepare rectangular and flat ingots of reasonable thickness. The compounding of the gallium arsenide and the ingot growth are generally achieved in an evacuated fused quartz ampul. Experiments for initial runs in the Thermco furnace produced ingots 6 by 1.5 by 0.5 inches. These were made in cylindrical, fused quartz ampuls with the ingot contained in a fused quartz boat lined with quartz cloth. The next size ingot prepared was 12 by 1.5 by 0.6 inches. It was also produced in a rectangular boat contained in a cylindrical ampul. Similarly, a rectangular shaped boat contained in a cylindrical ampul was used to produce an ingot 14 by 3.5 by 0.75 inches. The fabrication of a similar size ingot was attempted in a rectangular cross sectioned ampul. The ampul failed during evacuation because it was not strong enough to withstand the external pressure. Stress analyses of suitable ampuls for producing larger ingots were made and are presented later in this report. These analyses show that cylindrical ampuls with a reasonable wall thickness can withstand the collapsing pressure created by the vacuum to produce blanks for windows in sizes up to 12 by 6 by 0.5 inches. This size is about the practical maximum that can be achieved in an evacuated ampul. Therefore, in addition to evaluating ampul designs, different techniques for compounding gallium arsenide at atmospheric pressure were evaluated. A typical compounding ampul for atmospheric pressure is shown in Figure 3. This system uses flowing helium to produce a slight but constant back pressure in the ampul. The ampul is flushed with helium before it is heated. Helium flow is maintained during the compounding and growth cycle.

Various experiments were performed to compound and grow gallium arsenide at atmospheric pressure. Results were favorable and considerable effort was expended to perfect this process. Ingots up to 16 by 6.5 by 0.65 inches were produced by the atmospheric process. From these, windows as large as 12 by 6 by 0.41 inches were fabricated. They have good transmittance in the 2.5- to 12-μm wavelength region and do not show appreciable optical distortion.

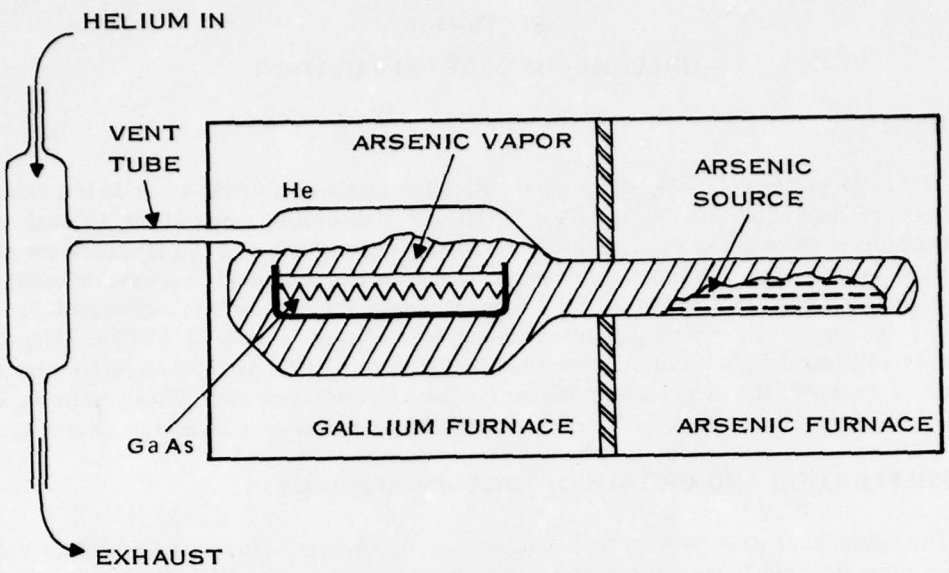

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Figure 3. Unsealed Ampul for Compounding and Growing Gallium Arsenide

During this program, a total of 34 compounding and ingot growth experiments were run. Nine of these were in evacuated ampuls and 25 were in the atmospheric type ampul. The experiments are summarized in Table 1.

C. AMPUL DESIGN AND FABRICATION

A typical evacuated cylindrical ampul for compounding and growing gallium arsenide ingots is shown in Figure 4. The ampul is made in two parts as shown. The boat containing the gallium is loaded into the left end. The right end is loaded with the arsenic and butted against the left end. Helium is passed slowly into the pump-down tube to prevent oxidation of the gallium and arsenic and the two parts are butt welded together with an oxy-hydrogen torch. The helium flow is shut off and the vent tube is sealed with the torch. The ampul is then evacuated to a pressure of less than 1 torr and the pump-down tube is sealed off by flame. After seal-off, the ampul is loaded into the furnace. The diameter of the arsenic end needs to be large enough to hold the required amount of arsenic to react with the gallium. For example, the 8-inch diameter chamber for the 6.5- by 14- by 0.7-inch ingot required an arsenic tube 2 inches in diameter by 30 inches long.

The size of an evacuated quartz ampul is limited by its collapsing strength. The collapsing strength of cylindrical ampuls is shown in Table 2.

TABLE 1. SUMMARY OF COMPOUNDING AND GROWTH EXPERIMENTS

Ingot No.	62	65	66	67	68	69
Furnace	Thermco	Thermco	Thermco	Thermco	Thermco	Thermco
Date	8-4-75	8-2-75	8-28-75	9-10-75	9-29-75	10-14-75
Ingot size inches	12 by 1.5 by 0.6	12 by 1.5 by 0.6	6 by 1.5 by 0.6	12 by 1.5 by 0.6	14 by 3.5 by 0.75	
Gallium Wt g	458	458	378	458	1542	
Arsenic Wt g	492	492	407	492	1658	
Chromium Wt g	0.080	0.080	0.065	0.180	0.80	
Gallium Oxide Wt g	0.475	0.475	0.393	0.475	2.4	
Excess Arsenic g	20	20	19	23	70	
Arsenic Temp. °C	620	620	620	620	618	
Cooling Rate °C/hr	0.6	0.5	0.5	0.5	0.35	
Temp. Gradient °C/in	0.8	0.8	0.8	1.0	0.67	
Growth Rate in/hr	0.75	0.63	0.63	0.5	0.52	
Ingot W g Theoretical	950	950	785	950	3200	
Ingot W g Actual						
Ampul Type	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	
Comments	Ga rich, cold spot in tunnel	T good over 10 inches some cloudy areas	Good T front half, rear cloudy, Ga rich	Cloudy temp., cycling in furnace	Ga rich, weighing error	

TABLE 1. SUMMARY OF COMPOUNDING AND GROWTH EXPERIMENTS (Continued)

Ingot No.	70	72	73	74	75	76	77
Furnace	Thermco	Thermco	Thermco	Thermco	Thermco	Thermco	Thermco
Date	11-9-75	11-13-75	11-21-75	12-1-75	12-9-75	12-16-75	2-2-76
Ingot Size inches	8 by 5 by 0.6	6.5 by 14 by 0.7	6 by 1.5 by 0.75	6 by 1.5 by 0.75	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7
Gallium Wt g		3061	285	285	2680	2680	2680
Arsenic Wt g		3289	346	346	3040	2940	2950
Chromium Wt g		1.6 g	0.150	0.160	4.6	4.6	4.6
Gallium Oxide g		4.8 g	0.450	0.450	5.6	5.5	5.5
Excess Arsenic g		71	40	40	160	60	70
Arsenic Temp. °C		623	610	610	614	615	6.5
Cooling Rate °C/hr		0.5	0.61	0.61	0.6	0.6	0.6
Temp. Gradient °C/in		0.6	1.22	1.22	1.2	1.55	1.2
Growth Rate in/hr		0.6	0.5	0.5	0.5	0.4	0.5
Ingot Wt g Theoretical		6350	591	591	5560	5560	5560
Ingot Wt g Actual					5515		
Ampul Type	Vacuum	Atmos.	Atmos.	Atmos.	Atmos.	Vacuum	Atmos.
Comments	Ampul failed on pump-down	Scrap Ga, No T, Ga rich	Ga rich, vent tube cracked	Ga rich, vent plugged, T in 8 to 14μm	Fast cool, vent tube broke, Ga rich	Ampul shifted, wedge shaped, Ga rich 8 inch dia. ampul	Vent cracked, fast cool, Ga rich, tail front good T

TABLE 1. SUMMARY OF COMPOUNDING AND GROWTH EXPERIMENTS (Continued)

Ingot No.	78	79	80	81	82	83	84
Furnace	Thermco	Thermco	Globar	Globar	Globar	Globar	Globar
Date	1-7-76	2-2-76	2-9-76	2-12-76	2-20-76	3-9-76	3-16-76
Ingot Size inches	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7
Gallium Wt g	Rerun of	Rerun of ingots	Rerun of	Rerun	2780	Rerun	Rerun
Arsenic Wt g	No. 75	Nos. 78, 73, 62	No. 79	of No. 80	3088	of No. 82	of No. 83
Chromium Wt g	0.5	None added	None added	None added	4.0	None added	None added
Gallium Oxide Wt g	1.0	None added	None added	None added	5.5	None added	None added
Excess Arsenic g	100 g added				100	950 g added	550 g added
Arsenic Temp. °C	620				600–640	600–730	615
Cooling Rate °C/hr	0.6				Not controlled	Fast cool	Not controlled
Temp. Gradient °C/in	1.2				2.1		1–1.5
Growth Rate in/hr	0.5						Erratic
Ingot Wt g Theoretical					5768	5860	5860
Ingot Wt g Actual					4920	5325	4900
Ampul Type	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.
Comments	First 8 inches good T–polished 6x8 piece rear, Ga rich	Leak in ampul. Run shut down near M.P.	Vent plugged and ampul broke	Vent plugged Shut down. GaAs was melted	Ga rich, As temp. low	Vent plugged, Ga rich	Ga rich, Front one-half polished

TABLE 1. SUMMARY OF COMPOUNDING AND GROWTH EXPERIMENTS (Continued)

Ingot No.	85	86	87	88	89	90	91
Furnace	Globar	Globar	Globar	Globar	Globar	Thermco	Globar
Date	4-5-76	4-13-76	4-21-76	5-3-76	5-18-76	5-19-76	5-24-76
Ingot Size inches	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 14 by 0.7	12 by 1.5 by 0.6	6.5 by 14 by 0.7
Gallium Wt g	Rerun of Ingots	2315	Rerun of No. 86	Rerun of No. 87	2763	Miscellaneous Precompounded	2748
Arsenic Wt g	Nos. 77, 84, 71	2585			2970	Material	3000
Chromium Wt g		0.120	0.270	None added	0.294	0.08	0.295
Gallium Oxide Wt g		0.240	0.480	None added	0.581	0.250	0.581
Excess Arsenic g	1500 g added	100	500 g added	100 g added	20	20 g added	47
Arsenic Temp. °C	610+	610+		610+	610+	630	600
Cooling Rate °C/hr	0.5	0.5		0.5	5.0	1.0	1.0
Temp. Gradient °C/in	1–1.5	1–1.5		1–1.5	1–1.5	0.5	1.1
Growth Rate in/hr	Erratic	0.3		0.5	5.0	1.0	1.0
Ingot Wt g Theoretical	6500	4800		4800	5713	1100	5701
Ingot Wt g Actual	5730	4315	3885				5475
Ampul Type	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Vacuum	Atmos.
Comments	Ga rich, Ingot cracked, froze top first	First time globars on top, Ga rich	Shut down, window broke	To Ga rich, As tube broke front polished	Vent tube cracked, Ga rich	Ingot and boat broken	Ga rich, AS temp too low

TABLE 1. SUMMARY OF COMPOUNDING AND GROWTH EXPERIMENTS (Continued)

Ingot No.	92	93	94	95	96	97	98
Furnace	Thermco	Globar	Thermco	Thermco	Thermco	Thermco	Thermco
Date	6-1-76	6-2-76	6-8-76	6-14-76	6-16-76	6-23-76	6-28-76
Ingot Size inches	6.5 by 14 by 0.7	6.5 by 14 by 0.7	6.5 by 16 by 0.7	6.5 by 16 by 0.7	6.5 by 16 by 0.7	6.5 by 16 by 0.7	6.5 by 16 by 0.7
Gallium Wt g	2748	2748	3045	Rerun of	Rerun of	Parts of Ingots No.	Parts of Ingots No.
Arsenic Wt g	3000	3000	3370	Ingot 94	Ingot 95	66, 88, 90, 91	84, 93
Chromium Wt g	0.295	0.320	0.320	0.770	0.770	0.237	5.0
Gallium Oxide Wt g	0.581	0.650	0.650	0.950	0.950	0.400	3.0
Excess Arsenic g	47	47	98	113	20	230	488
Arsenic Temp. °C	600	630	575	575	620+	600	625
Cooling Rate °C/hr	1.0	1.0	4.0	1.0	1.0	1.0	1.0
Temp. Gradient °C/in	1.1	1–1.5	1.1	1.4	1.0	0.65	1.0
Growth Rate in/hr	1.0	1.0	3.6	0.71	1.0	1.5	1.0
Ingot Wt g Theoretical	5701	5701	6317	6200	6300	6700	6565
Ingot Wt g Actual	5475	5420	6080	5830	6235	6000	6500
Ampul Type	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.
Comments	Ga rich, As temp too low	Ga rich, vent plugged	As tube cracked, fast cool	Ga rich	Best to date, polished	Ga rich, As temp too low	Good T

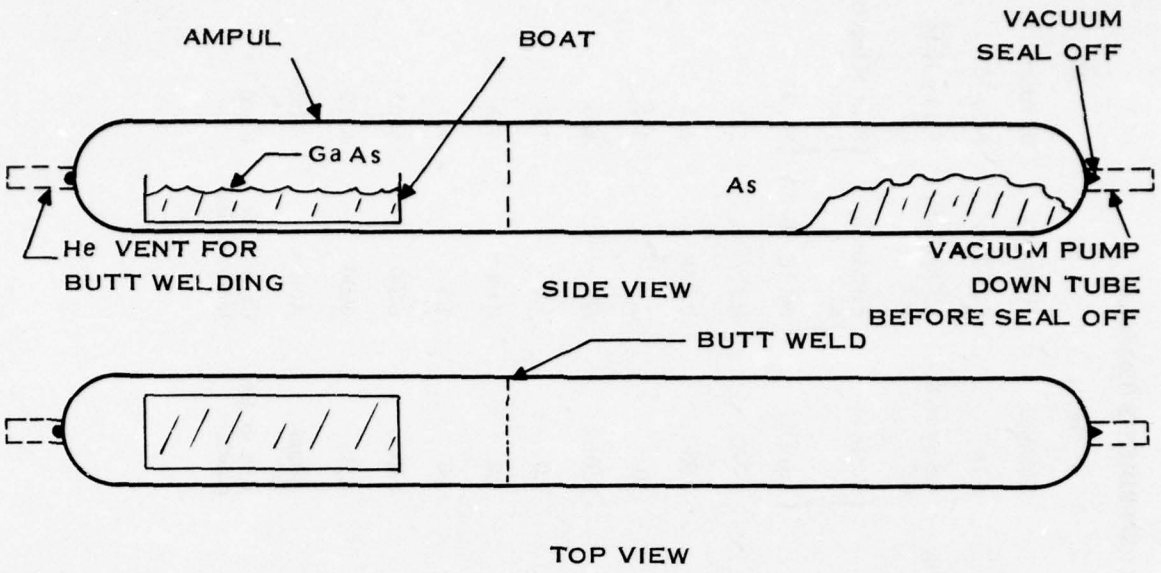

Figure 4. Sealed Ampul for Compounding and Growing Gallium Arsenide–Cross Section View

TABLE 2. COLLAPSING STRENGTH OF CYLINDRICAL AMPULS

Cylinder Diameter (in.)	Collapsing Pressure (psi) at Different Wall Thicknesses (in.) 0.1	0.15	0.20
4	330	1100	2530
5	170	570	1330
8	41	140	330

The Table 2 results indicate that all three thicknesses will withstand much more than the 14.7 psi collapsing pressure produced by the atmosphere when the cylinder is evacuated. Cylinders larger than 8 inches in diameter are expensive, difficult to mount in a furnace, and require an abnormally large diameter ampul and furnace relative to the width of a plate that can be produced in it.

Cylinders are relatively strong in comparison to their wall thickness because a collapsing pressure produces a compression stress in the wall. Brittle materials such as quartz break under tensile stress, which is generally lower by a factor of 10 over their compressive strength.

TABLE 3. STRESSES IN LARGE RECTANGULAR-SHAPED AMPULS

Plate Size (in.)	Maximum Stress (psi) for Various Thicknesses (inches)							
	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
3.5 by 15	9,200	2,300	1,020	600				
2.5 by 15	4,700	1,172	520	300				
7.5 by 15		9,200		2,300	1,470	1,020	750	
13 by 21		30,000		7,400		3,310		1,200

Rectangular cross-section ampuls have low collapsing strengths because the flat surfaces deform under the atmospheric load, placing the inside surface under a tensile stress and, therefore, susceptible to breakage. Using the "clamped edge" formula, stresses were determined for various sizes and thicknesses of quartz plates that would be used in the construction of large ampuls. Calculations were based on a plate loading of 14.7 psi as shown in Table 3; since the safe working stress for quartz is 1,000 psi, these results show that it is impractical to build rectangular, straight sided ampuls in large sizes. The required quartz thickness, 0.4 inch or greater, will make them expensive as well as difficult to fabricate. However, the stresses can be minimized by making the large faces a section of the cylinder. The stresses in such a design were analyzed. The results of this analysis are summarized in Appendix A and indicate that a wall thickness of 0.5 inch would be required to produce a 6.5- by 14-inch ingot. It would be difficult and expensive to reliably fabricate ampuls with this wall thickness.

For evacuation tests, two ampuls large enough for a 6.5- by 14-inch ingot were constructed using tubing split along its longitudinal axis. In one case, the split tubing was welded together, forming corrugated surfaces running the length of the ampul. In the other case, the corrugations ran the width of the ampul. In the first, the tubing wall thickness was 5 mm and in the second the wall thickness was 3 mm. Both were tested under vacuum and failed.

One 6.5- by 14-inch ingot was successfully produced in an 8-inch evacuated ampul. No further effort was expended on evacuated ampul design. Various ampuls were designed and fabricated for the atmospheric pressure compounding and growth process. The first runs were made in the Thermco furnace and the ampuls were similar to the one shown in Figure 3. Figure 5 is a cross-sectional view of this ampul. It was difficult to keep the vent tube from filling with arsenic at the exit from the furnace. Tubes up to 1 inch in diameter were used at this point but it was still difficult to keep the arsenic from plugging the vent tube. The helium back pressure could have been increased with the risk of ballooning the ampul. It was decided to improve the ampul design to better control the arsenic vapor. Partial control could be obtained by periodically heating the vent tube with a torch to vaporize the condensed arsenic, forcing it back into the ampul. The horizontal vent tube required complete vaporization of the arsenic to move it back into the ampul. It was also easy to crack the vent tube with the torch if there was too much arsenic condensed since arsenic has a much higher expansion coefficient than quartz.

During the course of the program the heating element in the Thermco furnace had to be replaced and hence the furnace was inoperable for an extended period of time. To continue ampul design studies, a Globar heated resistance furnace was designed, fabricated and installed in the gallium arsenide facility. Nine different ampul designs were evaluated using this furnace. All ampuls were designed for 6.5- by 14-inch ingots.

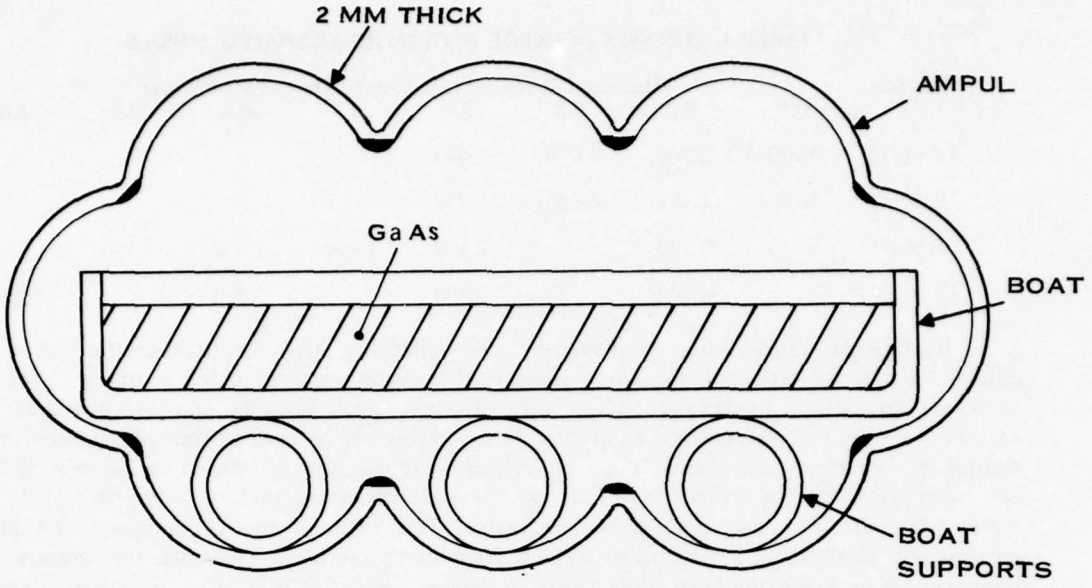

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Figure 5. A Typical Evacuated Cylindrical Ampul for Compounding and Growing GaAs Ingots

D. EXPERIMENTAL RESULTS

The following results are discussed as a function of ampul design. Each ampul was open to a helium atmosphere rather than the customary evacuated chamber.

1. Ampul No. 1

Figure 6 shows the ampul used in Run No. 79. The ampul was fabricated such that Globar heating elements were an integral part of the ampul. These heating elements were housed in "ports" fabricated from quartz tubing. The quartz tubing traversed the width of the ampul, hence the heating elements were in the middle of the ampul. The quartz boat rested directly on the quartz tubing.

The ampul was tested using precompounded gallium arsenide. However, a crack in the ampul forced a premature shutdown of the run. Due to the difficulty in fabricating an ampul of this design, no further attempts were made to evaluate this design.

2. Ampul No. 2

Figure 7 shows the ampul designed for Run No. 80. In this design, the ampul was supported above the Globars on silicon carbide plates. The Globar heating elements were external to the ampul rather than an integral part of the ampul.

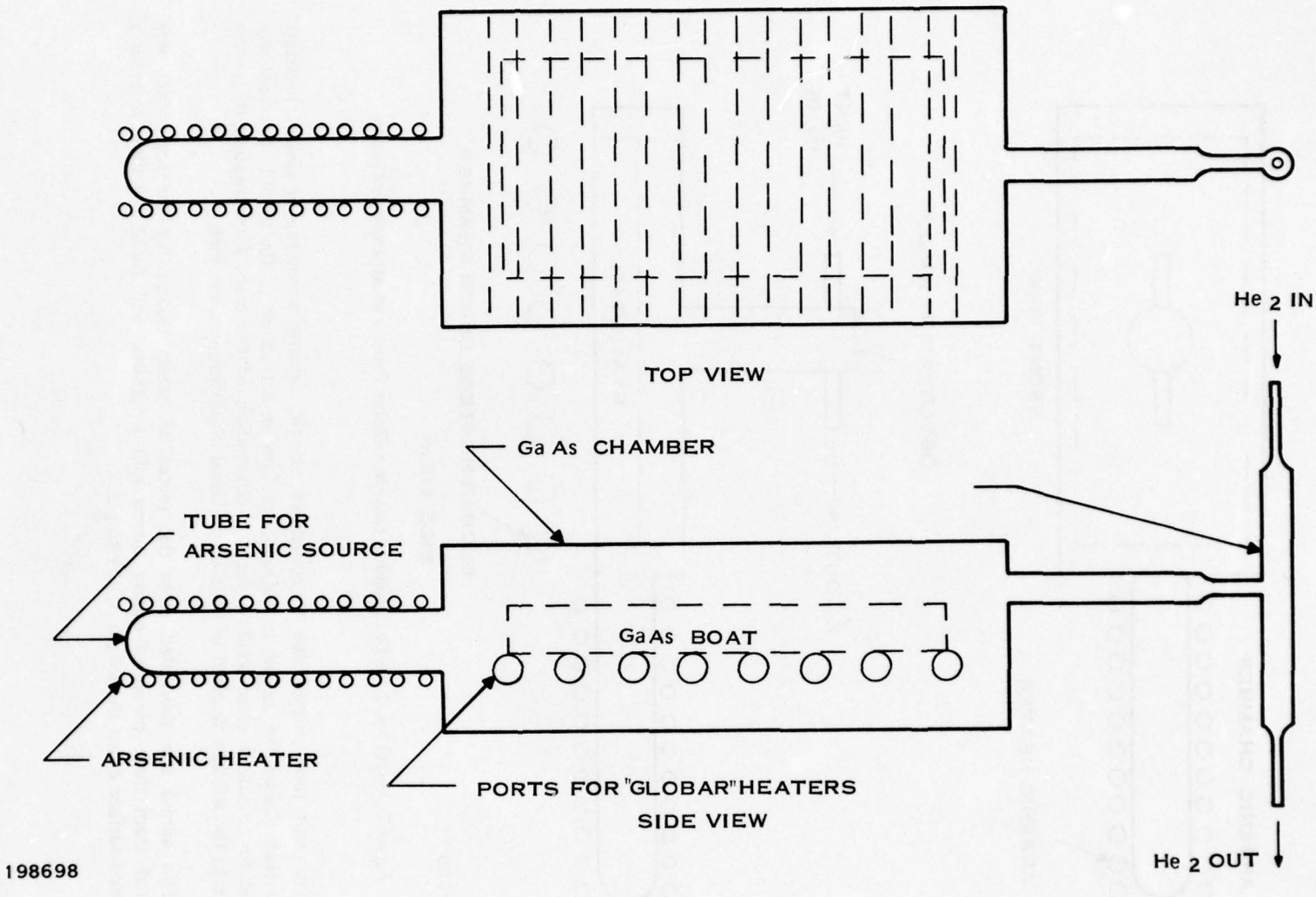


Figure 6. Ampul No. 1 for Compounding GaAs at Atmospheric Pressure in Globar Furnace

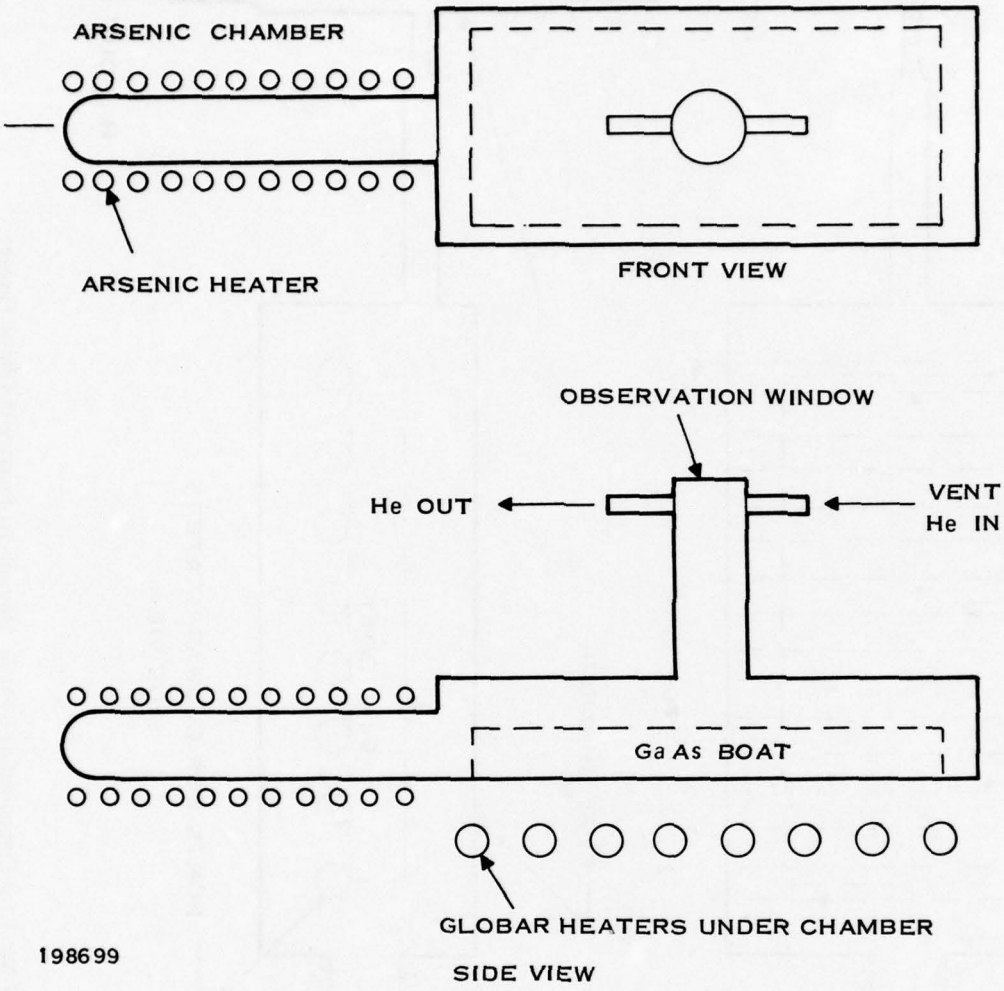


Figure 7. Ampul No. 2 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

The vent tube clogged due to condensed arsenic, causing a buildup of arsenic pressure. This in turn caused the ampul to balloon, resulting in a fracture of the ampul. The vent was designed to provide a clear window for the observation of the melt. Condensation of arsenic vapor onto the window resulted in little or no visual observation of the melt.

This ampul was fabricated from flat pieces of quartz except for the top which was fabricated from three pieces of quartz tubing split lengthwise and fused together, forming a corrugated surface down the length of the ampul.

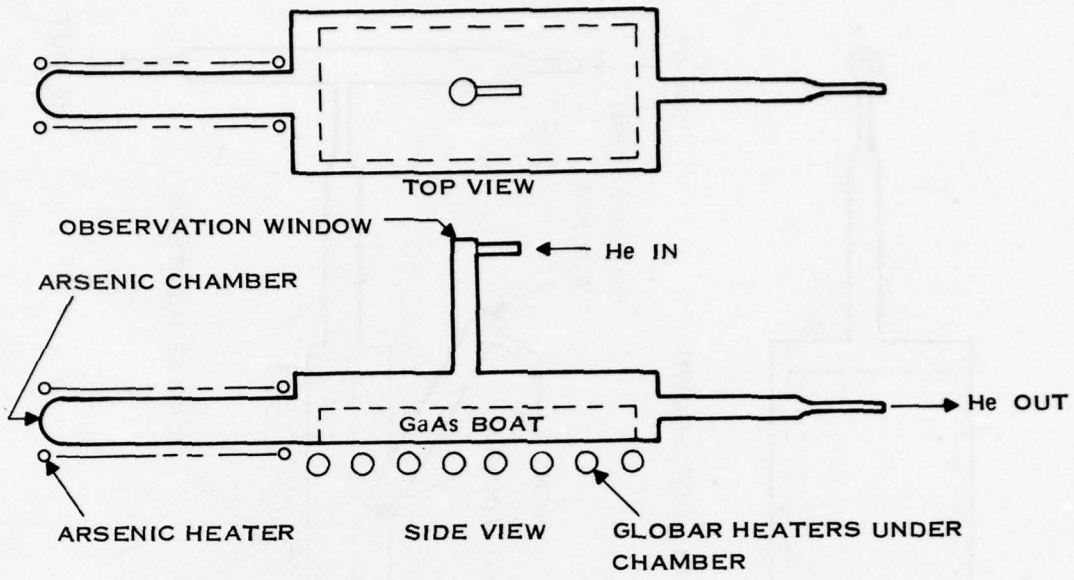


Figure 8. Ampul No. 3 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

3. Ampul No. 3

Figure 8 depicts the ampul used in Run No. 81. This ampul was similar to ampul No. 2 and was another attempt to provide a clear window to observe the gallium arsenide melt. The viewing port remained clear but too much arsenic was transported to the exit tube and condensed. This again caused the vent to break and the run was aborted.

4. Ampul No. 4

Figure 9 shows the design of the ampul used in Run No. 82. It consisted of two arsenic source tubes, two vent tubes and a viewing port mounted at an angle. The viewing tube had a window on each end. The window inside the ampul collected condensate even though the air inside the tube provided some thermal insulation. Two vents were used in an attempt to solve the condensed arsenic problem. Both vents remained open, the ampul remained intact and the ingot was flat. However, there were cold spots in the arsenic source furnace, resulting in enough condensed arsenic to render the ingot gallium rich.

5. Ampul No. 5

Ampul No. 5 is shown in Figure 10 and was used for Run No. 83. It consisted of an external flame heated window, a helium vent tube and an arsenic chamber. The temperature controller for the arsenic heater failed, causing an increase in arsenic vapor pressure and subsequently a ballooning of the ampul. The ingot was gallium rich so the ballooning was attributed to the expansion of both arsenic and helium.

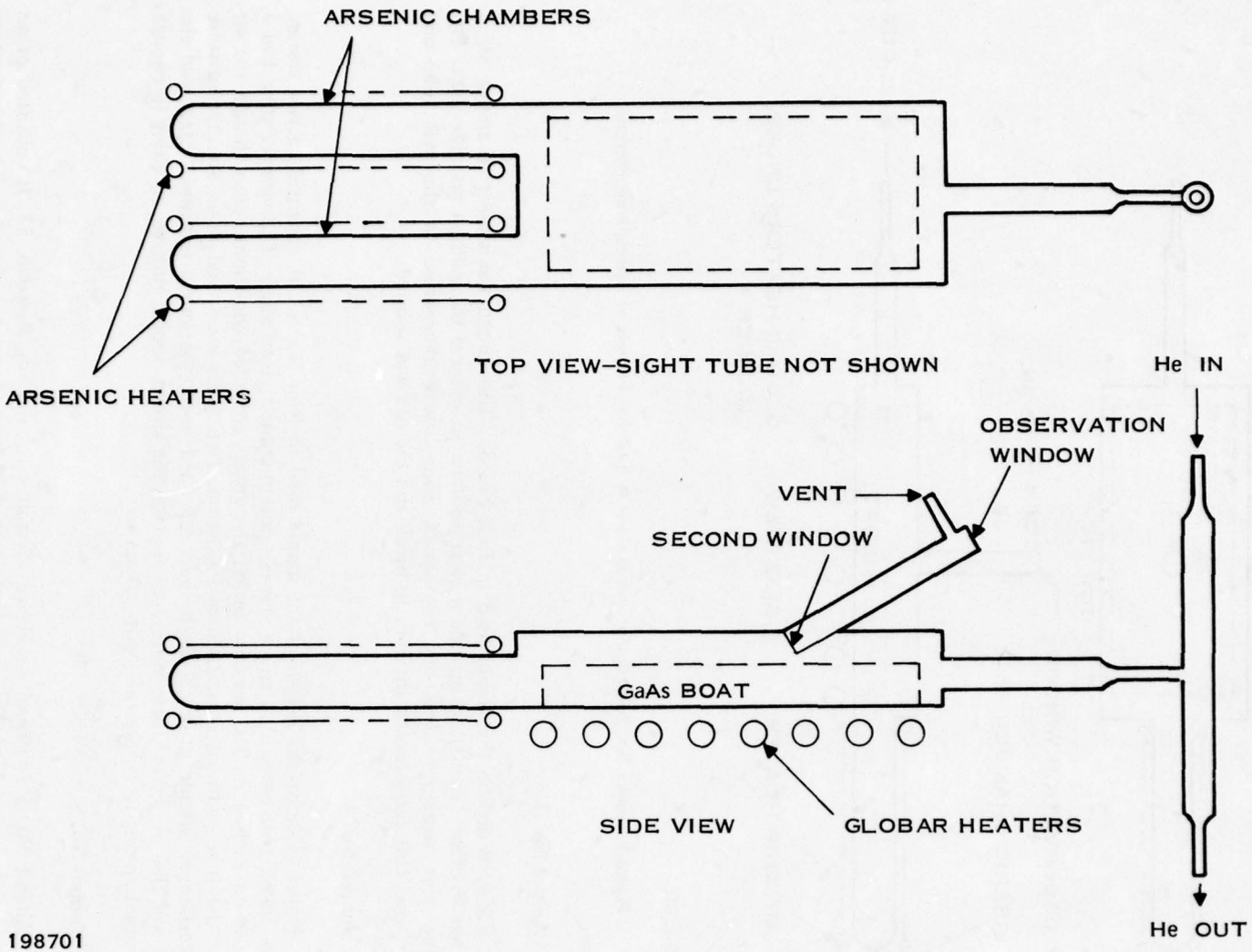


Figure 9. Ampul No. 4 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

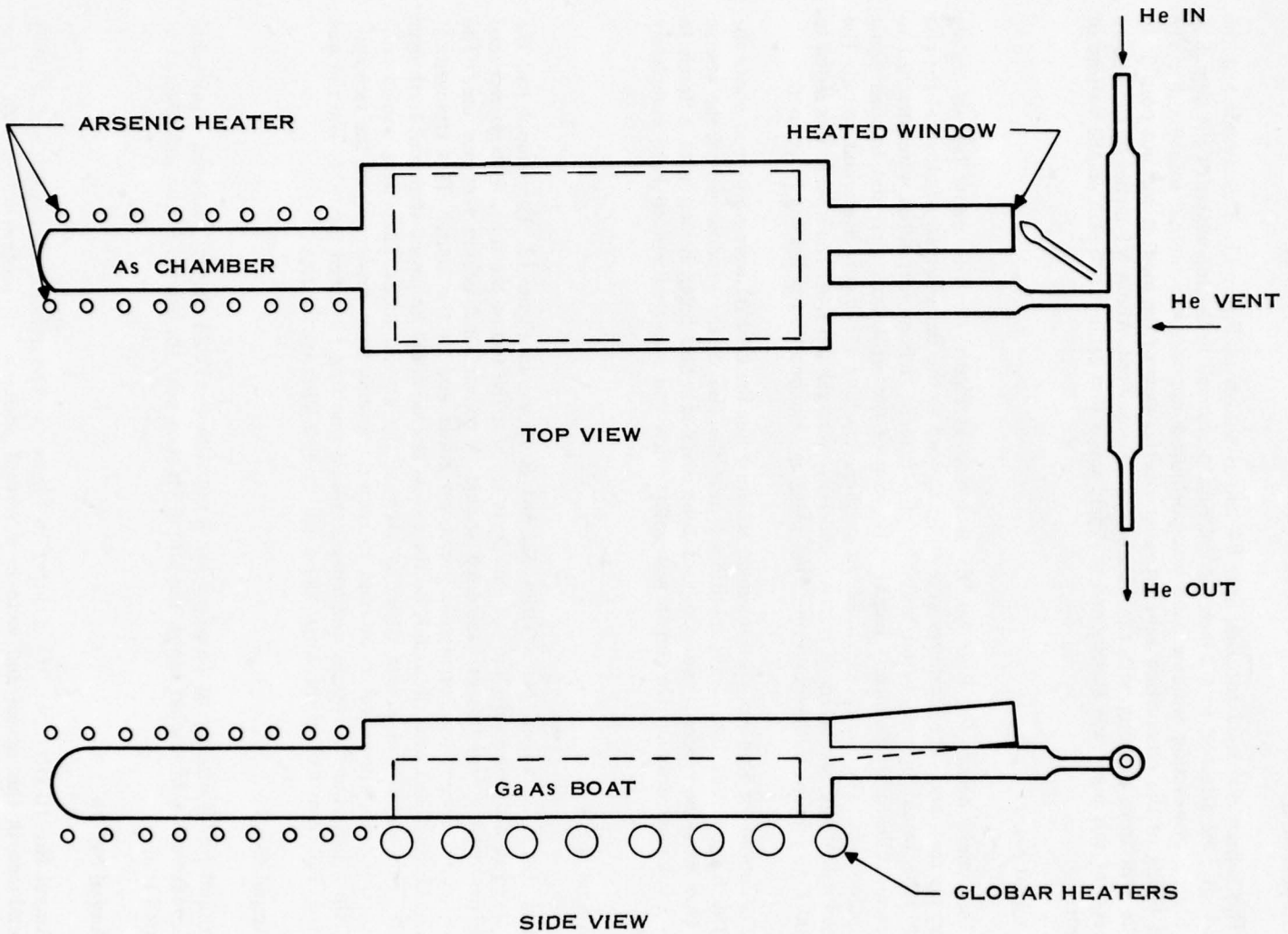


Figure 10. Ampul No. 5 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

6. Ampul No. 6

This design was used for Run No. 84 and is shown in Figure 11. This ampul had the helium vent tube attached to a 2-inch vertical tube positioned in the top center of the ampul. A flame heated observation window tube was positioned opposite the arsenic source tube. The upward tilting of the observation tube provided a better view of the melt. It was not possible to keep the vent from plugging with this helium vent arrangement. About 8.5 inches of the first to freeze end of this ingot was stoichiometric. There was a thin gallium rich skin on the bottom of the ingot.

7. Ampul No. 7

The ampul design for Run No. 85 is shown in Figure 12. The ampul has an arsenic chamber on each end. The chambers were tilted upward so the flame-heated windows at the end of each tube would provide better visibility of the melt. Helium vent tubes were attached to each arsenic tube near the main chamber. The top of the ingot froze first and trapped liquid GaAs underneath. The liquid expanded on cooling, cracking the ingot, boat, and ampul. The ingot had essentially two layers of material and both were gallium rich. The arsenic was raised to only 600°C to prevent the helium vents from plugging. Apparently, top heating is required.

The ampul for Run No. 86 was similar to No. 7 but the Globars were positioned above the melt. The helium vent tubes were positioned near the end of the window end of the arsenic tubes. One window cracked and one vent tube cracked while being heated with a torch to remove condensed arsenic. The ingot was gallium-rich and appeared not to have completely melted.

8. Ampul No. 8

The design of ampul No. 8 (Run No. 88) is shown in Figure 13. This ampul had the arsenic tubes turned downward and the viewports are near the top of the tube. A flame was used to keep the viewing area free of condensed arsenic. A conventional helium vent was used. The last two ampul designs had an arsenic source on either end of the ampul. This arrangement permitted heating each one alternately so the excess arsenic could be passed back and forth over the melt. This ampul had a cold finger in each of the arsenic tubes. They were cooled with nitrogen. This arrangement was an attempt to keep the arsenic from condensing on the viewport. It did help a little but the arsenic condensing around one finger cracked the tube. The run was completed. The front half of this ingot had a gallium-rich layer on the top.

9. Ampul No. 9

Ampul No. 9 was similar to ampul No. 8 but with the "cold fingers" removed. Again, due to the condensation of arsenic vapor, the ampul cracked near the arsenic source and resulted in an aborted run.

10. Ampul No. 10

Ampul No. 10 (Run No. 91) is shown in Figure 14. The arsenic tubes and the vent tubes were combined in this design and were in a vertical position. The portion of the wall of the tubes was used for the windows and they were heated with a torch to prevent arsenic

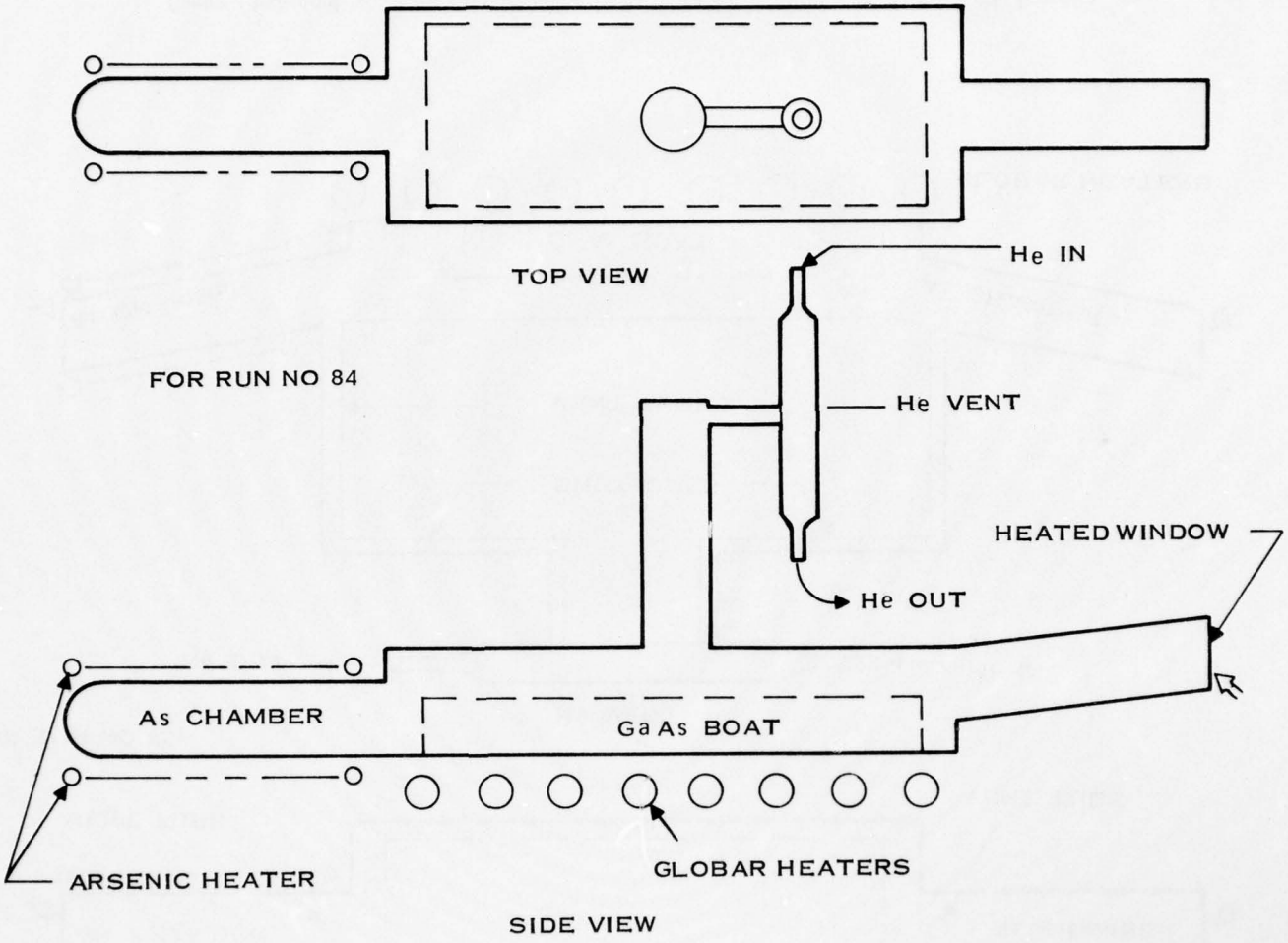


Figure 11. Ampul No. 6 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

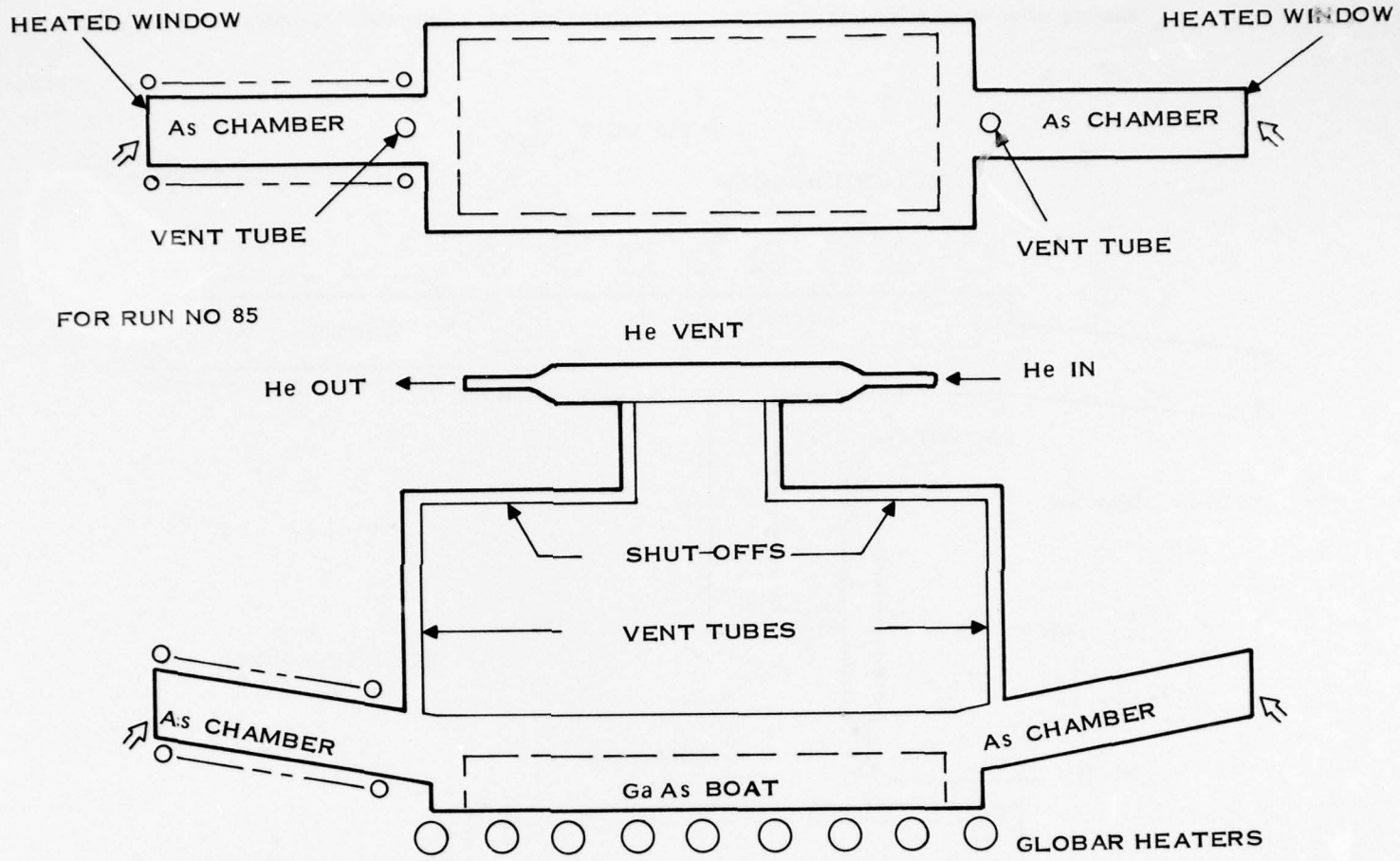


Figure 12. Ampul No. 7 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

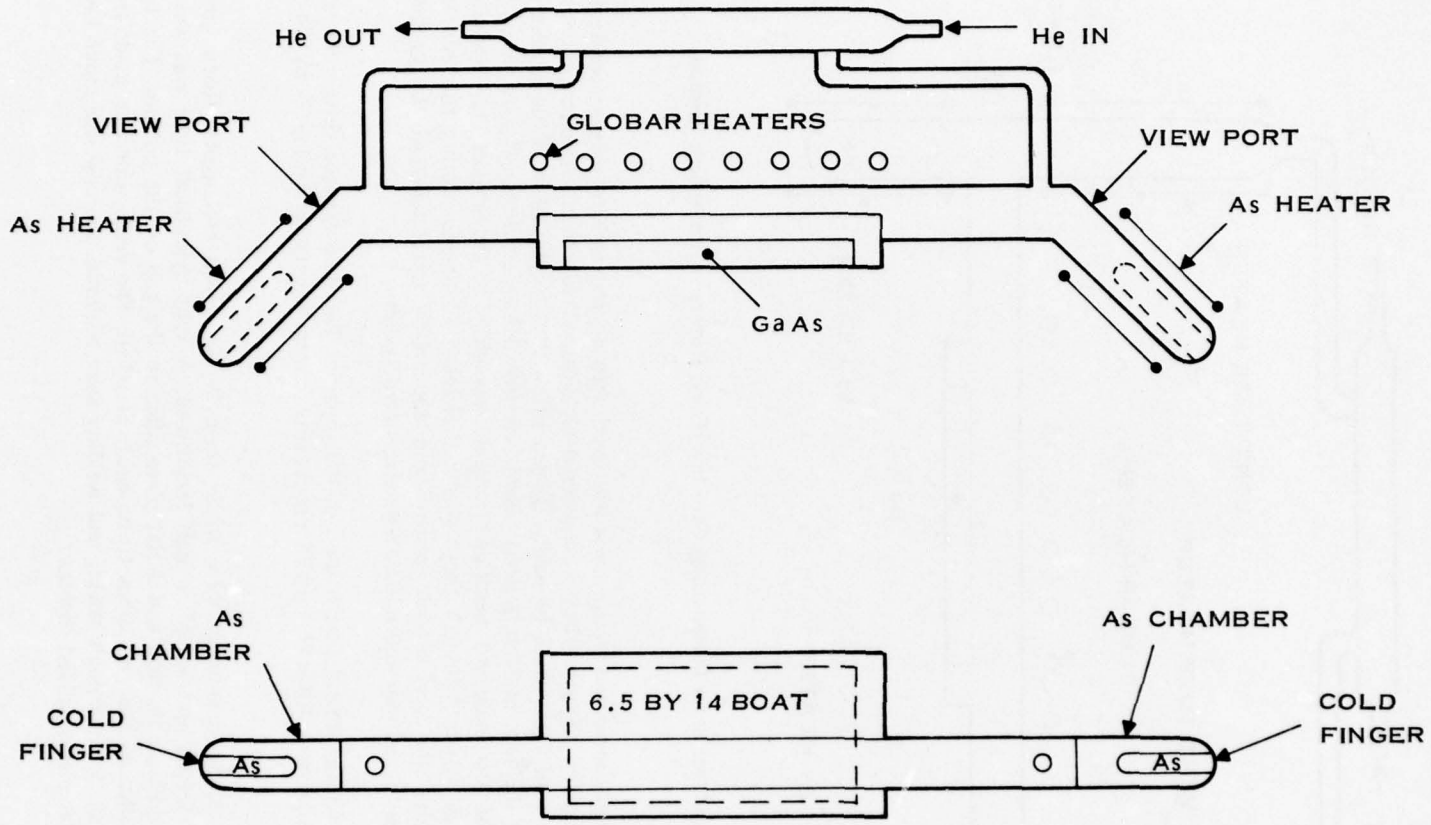


Figure 13. Ampul No. 8 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

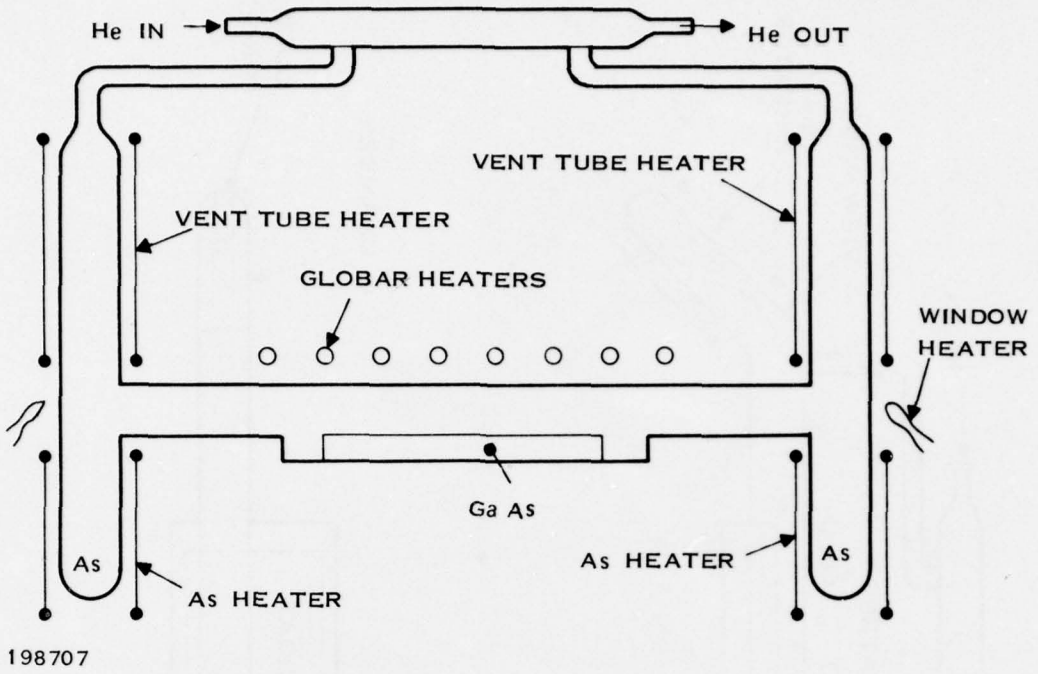


Figure 14. Ampul No. 10 for Compounding GaAs in a Globar Furnace at Atmospheric Pressure

condensation. The bottom of the arsenic tube was lined with quartz cloth to prevent condensing arsenic from breaking the tubes as they were alternately heated and cooled. Arsenic condensing near the top of the vent tube could be easily flamed off with a torch. All available arsenic was compounded during the run, indicating good arsenic control. However, during the set up of this run, a weighing error was made and insufficient arsenic was added to the ampul. This resulted in a slightly gallium-rich ingot. Although there was a deficiency of arsenic during this run, this ampul design provided the best arsenic control and appears to solve many of the problems associated with preparing gallium arsenide in a nonevacuated system.

Figure 15 shows the ampul design used in the repaired Thermco furnace. Five runs were made using this design and Runs 96 and 98 produced excellent ingots measuring 7- by 14- by 0.5-inches.

The last five ampul chambers were made from 2- by 6-inch rectangular fused quartz tubing. The desired length was sawed in half lengthwise. A split cylindrical tube was welded between the two pieces on the top and a flat plate filled in the gap on the bottom. The tube section on the top allowed the end tubes to be easily attached. The boats were also made from the rectangular tubing. Even though sawing and welding were required, the cost was much lower than trying to use flat plates welded together.

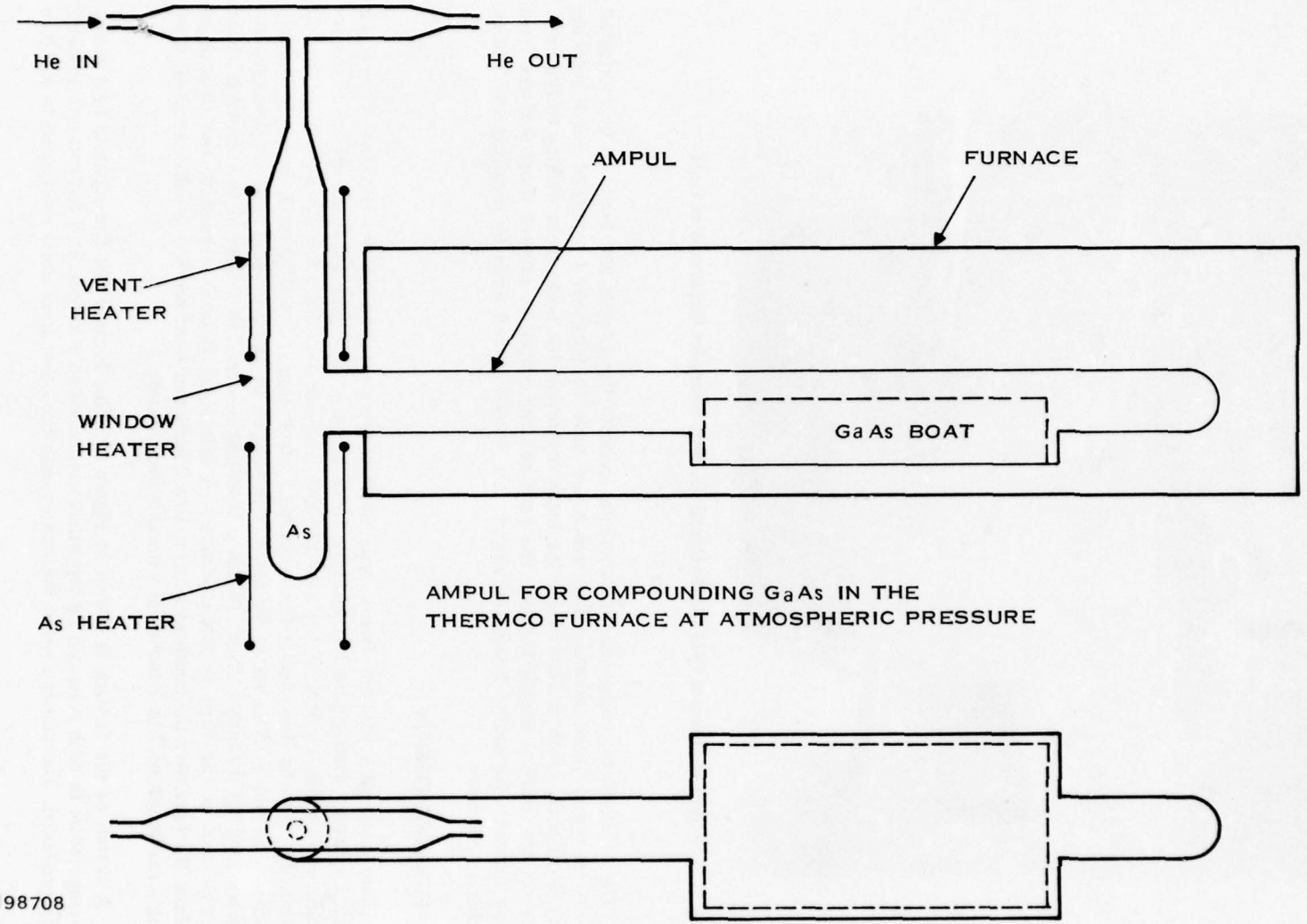


Figure 15. Ampul for Compounding GaAs in Thermco Furnace at Atmospheric Pressure

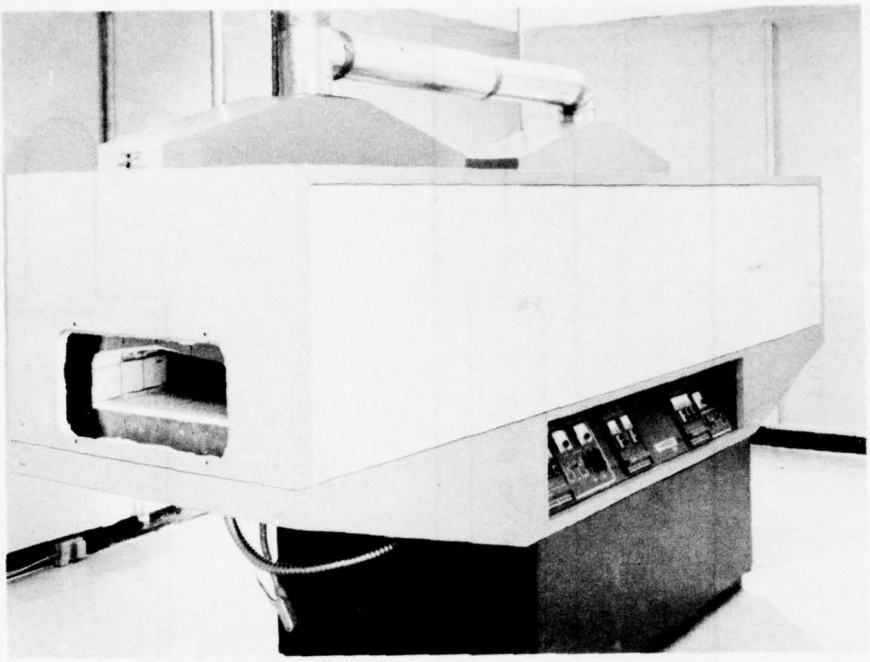


Figure 16. Furnace Used for Horizontal Gradient Freeze for Preparation of GaAs

The atmospheric compounding technique permits the ampuls and boats to be fabricated from 2- to 3-mm fused quartz parts which are easy to fabricate by normal torch working techniques. Quartz cloth is used to line the boats to prevent the GaAs from sticking to the boat. A layer of the cloth is placed between the boat and the ampul to prevent those surfaces from sticking together. Generally, boats and ampuls can be used several times by repairing any breaks, reducing ampul costs.

E. FURNACE DESIGN

Two horizontal gradient freeze type furnaces were used during this program. One was a Thermco specially built gradient freeze type furnace, shown in Figure 16. It consists of two main sections, one for the control of the arsenic vapor pressure and the other for compounding and directionally freezing the melt. The arsenic control zone of this furnace is approximately 56 inches long and 5.75 inches in diameter. The melting or compounding zone is approximately 70 inches long by 17 inches wide. It has a D-shaped heater. The height in the center is about 9.5 inches and at the edge is about 6 inches. A refractory floor is needed in the furnace to distribute the load over the heating element; 1 to 2 inches of head room is usually required, thus, leaving a maximum of 7 to 8 inches of workable head room.

A sketch of the furnace is shown in Figure 17. This furnace has five separate heat zones. The temperature in each zone can be separately controlled so a longitudinal temperature gradient can be produced. The center zone is the master with the other four zones referenced to it. Once

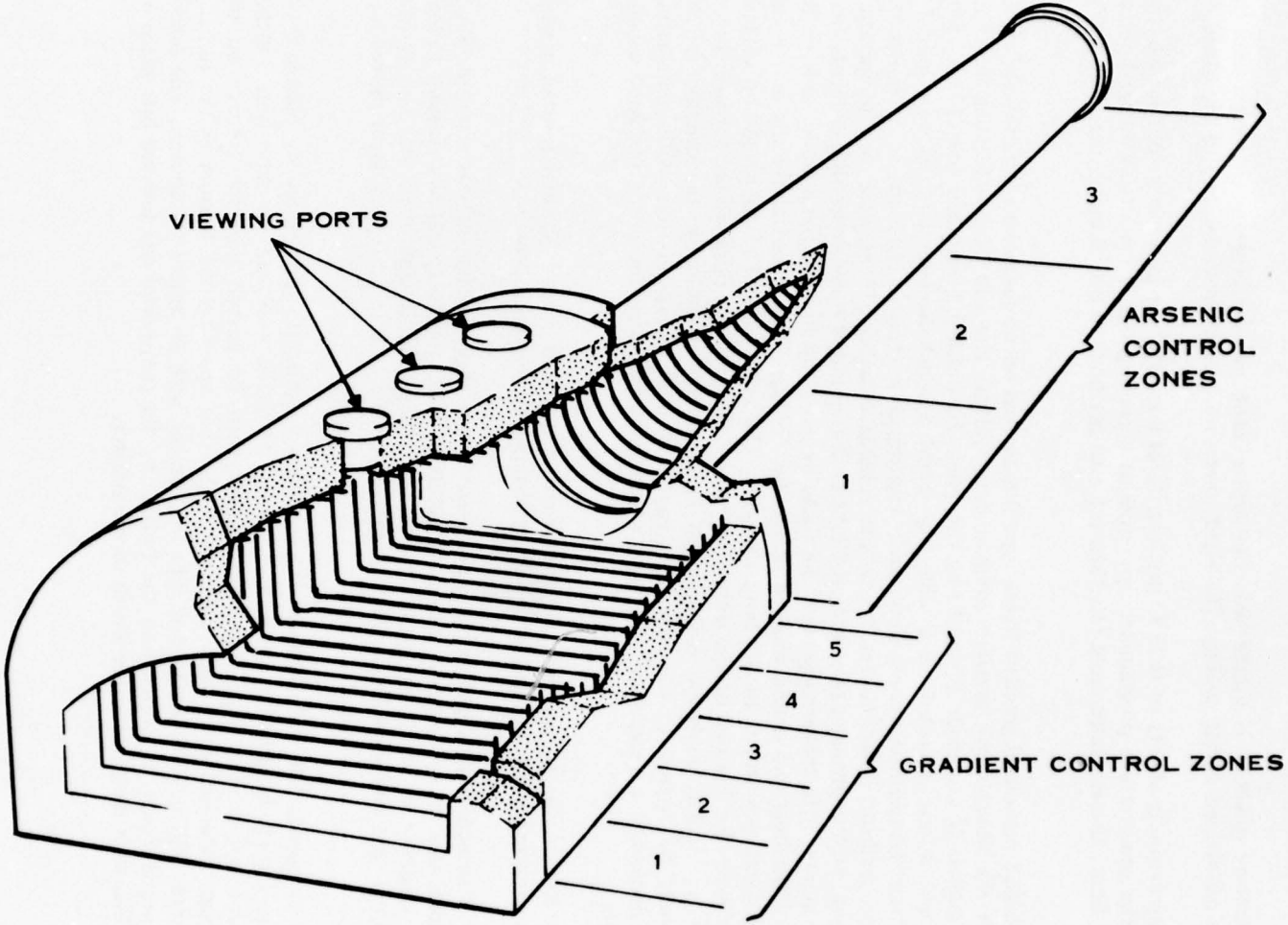


Figure 17. Temperature Zones in the Horizontal Gradient-Freeze Growth System

the temperature gradient is established, the center zone can be programmed down and the gradient is maintained during cooling. The ingot, therefore, freezes from one end to the other.

Temperature gradients of 0.25°C per inch to at least 2°C per inch can be obtained in this furnace. The temperature programmer can produce a cooling rate of about 0.4°C per hour to 4.4°C per hour. Growth rates from less than 0.5 inch per hour to over 4 inches per hour can be achieved.

A second horizontal gradient freeze type furnace was set up temporarily to evaluate ampul designs for the atmospheric pressure compounding system. The size of its chamber was 7 by 15 by 18 inches. It was made of insulating fire brick. Its outside dimensions were 17 by 25 by 28 inches and it was mounted on a table top. Eight 5/8-inch-diameter Globars were used for heaters. Four temperature controllers each controlled a pair of Globars so a horizontal temperature gradient could be set up in the furnace chamber. There were two temperature programmers, each controlling two pairs of Globars. During initial runs the heating elements were below the ampul. With this arrangement, the GaAs froze on top first, trapping liquid underneath. Breakage of the boat and ampul resulted. Later, the Globars were placed above the ampul and this arrangement was found to be more desirable. The ampul also had to be set on ceramic spacers to keep the bottom of the ampul about 1/2-inch off the floor of the furnace. Ingots 6.5 by 14 by 7 inches could be compounded in this chamber. Actually, the chamber of the furnace could be altered to accommodate changes in ampul configuration. With temperature control refinements, a furnace of this type would be satisfactory for producing good quality GaAs ingots.

The heaters for the arsenic chambers were made from wound Kanthal resistance wire. They were powered and controlled with SCR type temperature controllers.

The Thermco furnace performed well after the new heating element was installed. Slight modifications may be necessary for the manufacture of larger ingots. It will be necessary to load the main chamber of the ampul into the compounding furnace and then seal the vertical arsenic-helium vent chambers to the main ampul. Then the arsenic heaters could be moved into place.

The ampuls for the 6.5- by 16-inch ingots were loaded into the furnace by placing them on a silicon carbide holder that was 18 inches long, 11 inches wide and the sides were 3 inches high. It did not have a top. This holder could then be pushed into the furnace on the 1-inch-diameter alumina tubes that were placed 2 inches apart on the bottom of the furnace. Larger ampuls will have to be loaded into the furnace with an ampul transporter. The holder with the ampul would be carried into the furnace by the transporter and lowered into place on silicon carbide rails that extend the length of the furnace.

SECTION III

GALLIUM ARSENIDE CHARACTERIZATION

Considerable effort during the program was directed toward developing an atmospheric pressure gallium arsenide compounding system. There was not an opportunity to fully evaluate the consistency of the process because each ingot was slightly different.

A. TRANSMITTANCE

The transmittance of several ingots produced by the atmospheric pressure compounding process was measured. The transmittance of ingot No. 78 is shown in Figure 18. The transmittance of ingot No. 98 is shown in Figure 19. This was a delivery item on the contract. The transmittances of ingots No. 74 and No. 84 were measured. The doping was somewhat low, about 0.1 ppm chromium, and transmittance was degraded in the 8- to 12-μm wavelength range. Four 1.5 inch diameter by 0.2 inch thick transmittance samples of chromium-oxygen doped gallium arsenide were delivered to AFML. Transmittance is shown in Figure 20.

B. MODULATION TRANSFER FUNCTION

The modulation transfer function (MTF) of ingot No. 98 was determined by comparing the MTF of a standard lens cell to the MTF obtained by placing the flat plate between the light source and the standard lens cell. The plate was measured in both the horizontal (0-degree) and vertical (90-degree) positions. Assuming the standard lens cell to be 100 percent, the MTF of the plate was:

98.7 percent in the horizontal position and

95.7 percent in the vertical position.

C. ABSORPTION COEFFICIENT

Absorption coefficients (α) from 8 to 14 μm were determined for typical chromium-oxygen doped gallium arsenide using transmittance data from samples with varying thicknesses. The absorption coefficient was calculated using the relationship

$$\alpha(\mathrm{cm}^{-1}) = \frac{\ln \frac{T_2}{T_1}}{d_1 - d_2}$$

where

T_1 = Transmittance of sample whose thickness is d_1

T_2 = Transmittance of sample whose thickness is d_2

These results are shown in Table 4.

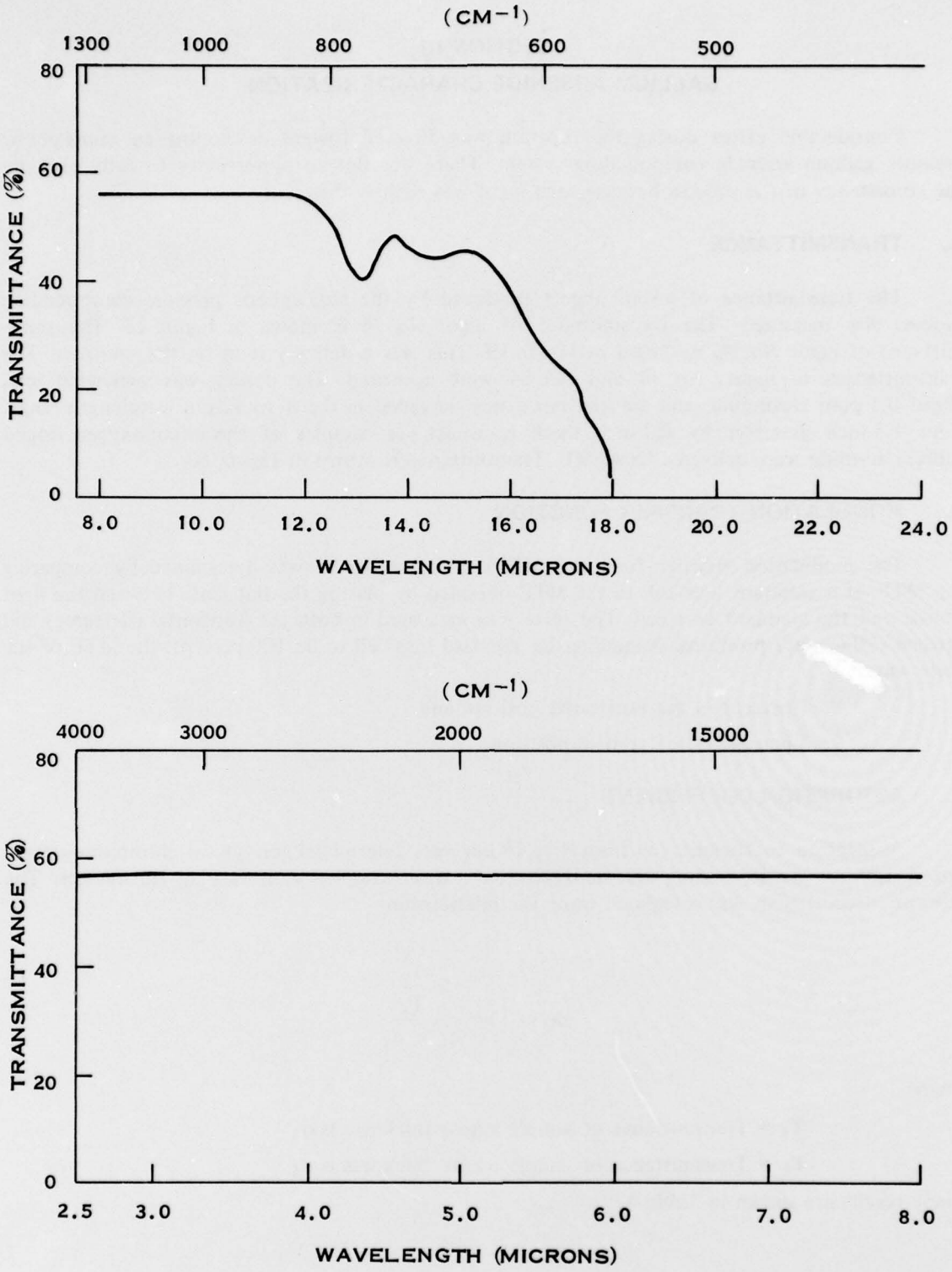
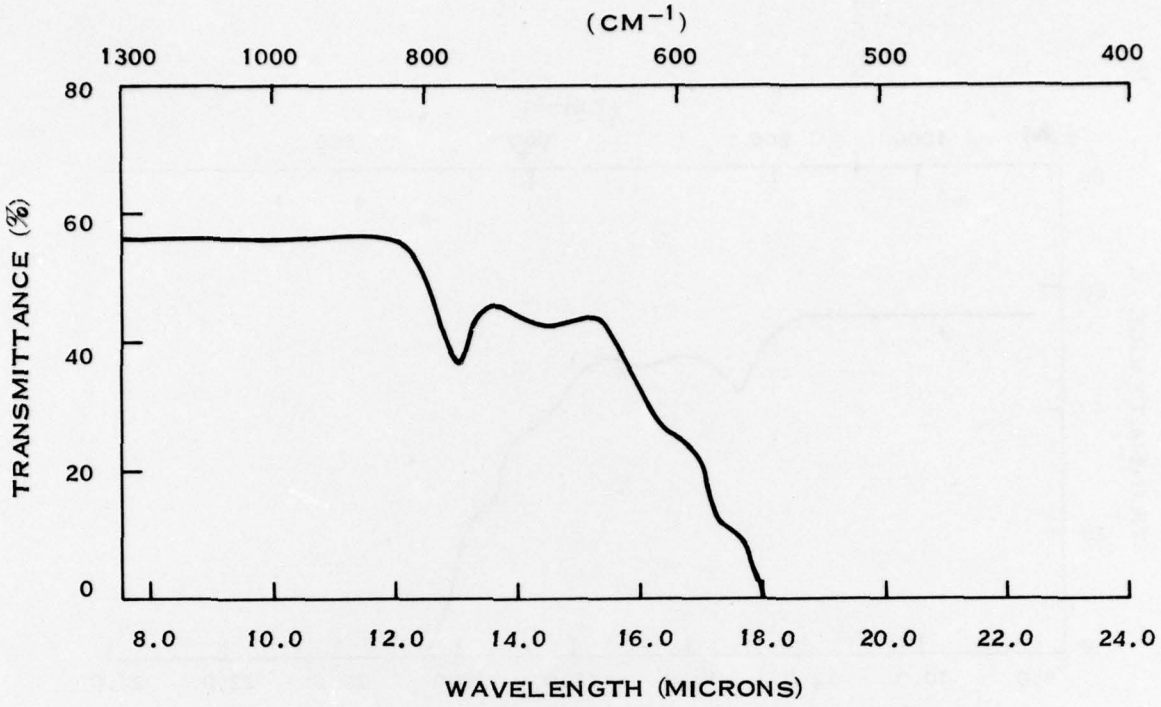


Figure 18. Transmittance of Ingot No. 78 for the Wavelength Range 2.5 to 18 μm



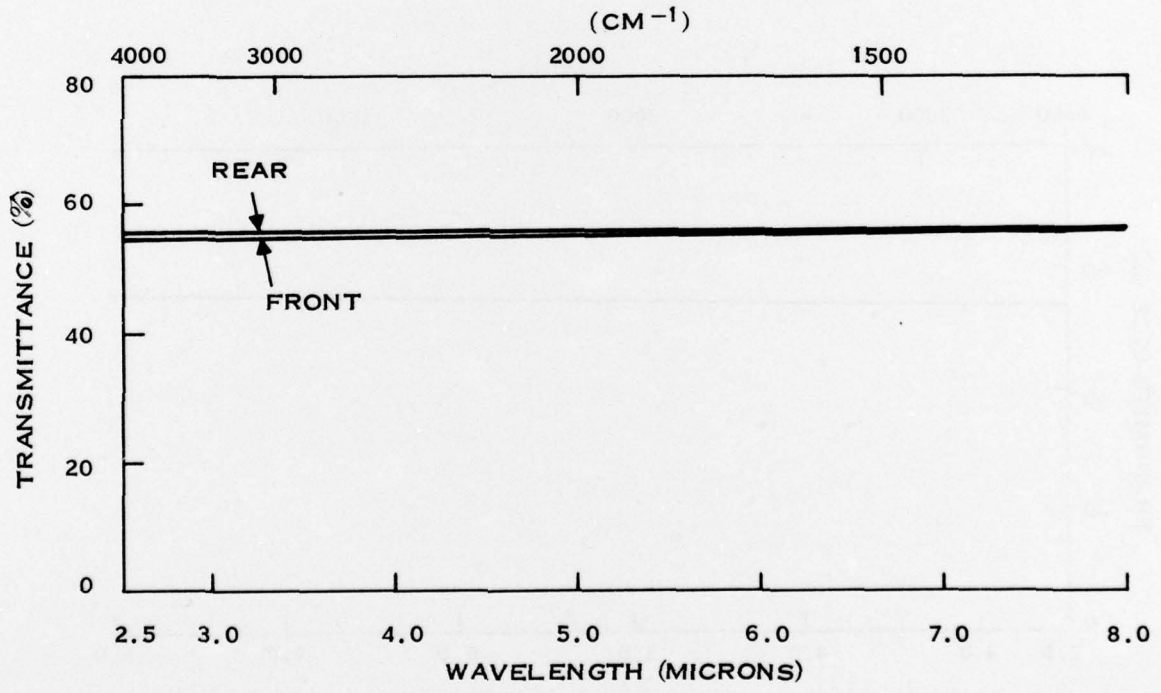


Figure 19. Transmittance of Ingot No. 98 Contract Delivery Sample

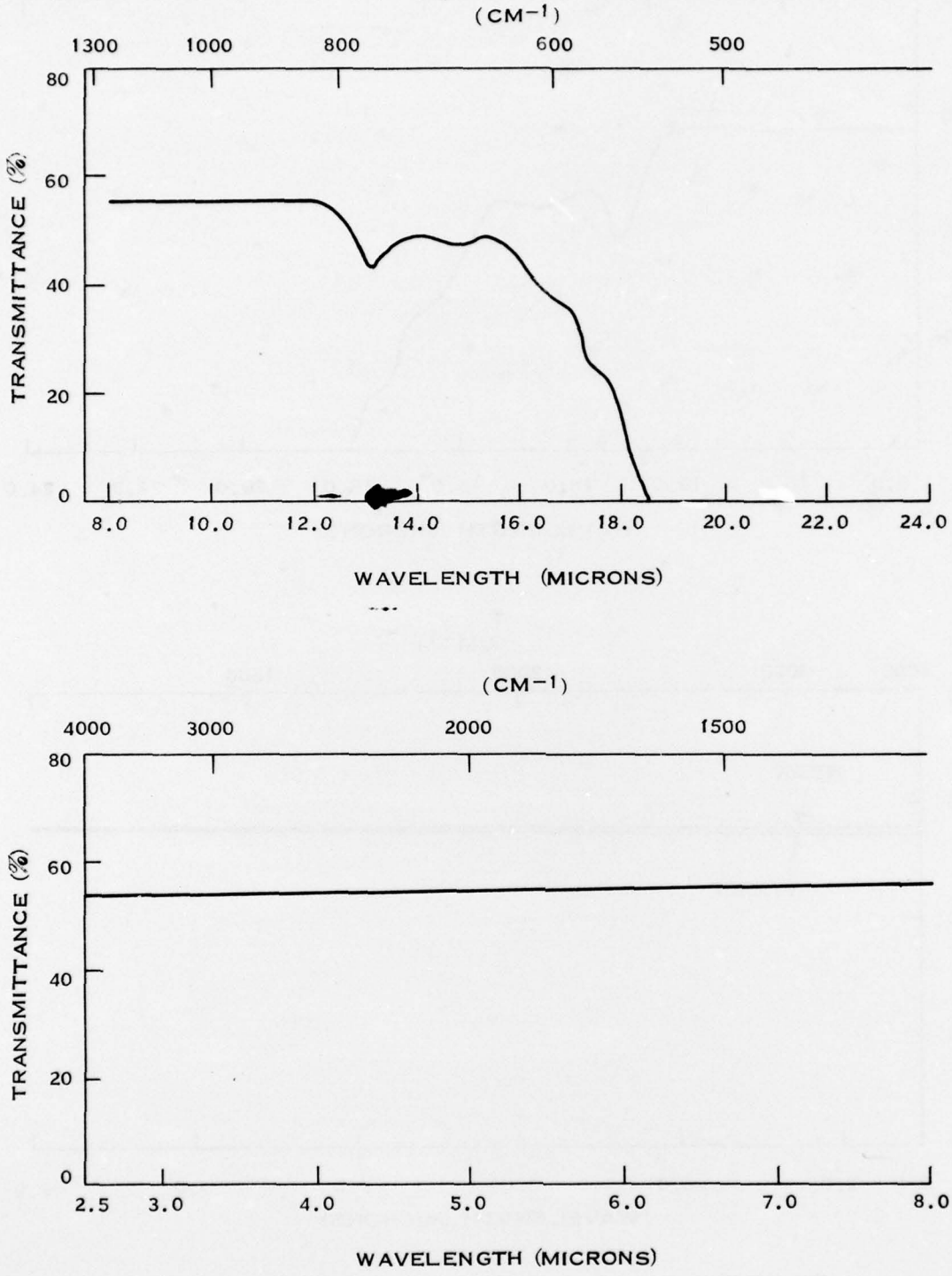


Figure 20. Transmittance of Rain Erosion Samples

D. THERMAL CHANGE IN REFRACTIVE INDEX FOR GALLIUM ARSENIDE

The change in refractive index of gallium arsenide as a function of temperature was determined[2] by fabricating a precise prism and then measuring the refractive index by standard optical techniques. The precision and accuracy of this method was confirmed by measuring a known silicon standard under the same conditions. The results of these measurements are shown in Table 5.

TABLE 4. ABSORPTION COEFFICIENT OF CHROMIUM OXYGEN DOPED GALLIUM ARSENIDE

Wavelength (μm)	α Absorption Coefficient (cm^{-1})
8	<0.01
9	<0.01
10	<0.01
11	<0.01
12	0.02
13	0.24
14	0.16

TABLE 5. THERMAL CHANGE IN REFRACTIVE INDEX FOR CHROMIUM-OXYGEN DOPED GALLIUM ARSENIDE

Wavelength (μm)	dn/dt*
3	157×10^{-6}/°C
5	152×10^{-6}/°C
8	150×10^{-6}/°C
10	148×10^{-6}/°C
12	144×10^{-6}/°C

*Measured from 77K to 300K

E. RAIN EROSION

Eight rain erosion samples 1.5 by 0.5 by 0.2 inches were submitted to AFML. Results have not been reported.

Transmittance of these samples is similar to the transmittance of the sample shown in Figure 20.

[2] A. Ray Hilton, unpublished work.

TABLE 6. PROPERTIES OF CHROMIUM-OXYGEN DOPED GALLIUM ARSENIDE

Property	Value
• Knoop hardness	725
• Refractive index (10 μm)	3.2778
• dn/dt (10 μm)	$148 \times 10^{-6}/°C$
• Modulus of rupture (psi)	10,400
• Absorption coefficient (cm^{-1}), (10 μm)	<0.01
• Density (g/cm^3)	5.319
• Expansion coefficient (in/in/°C)	5.70×10^{-6}
• Thermal conductivity W/cm-°C	0.35 ±0.04
• Operational temperature	>200°C

F. OTHER

The Knoop hardness, modulus of rupture, thermal conductivity and thermal expansion values of the samples produced on this contract are identical to those reported in AFML-TR-75-49. Table 6 summarizes the properties of typical chromium-oxygen doped gallium arsenide infrared optical material.

SECTION IV
SUMMARY AND CONCLUSIONS

The goal of the program to produce semi-insulating gallium arsenide in sizes up to 6 by 12 inches has been achieved. Figure 21 shows a photograph of a 6- by 12- by 0.4-inch polished gallium arsenide plate. Its transmittance is shown in Figure 19. The gallium arsenide was doped with the deep acceptor impurity chromium to reduce free carrier absorption, even at temperatures as high as 200°C. In addition, oxygen in the form of Ga_2O_3 was added to the melt to render some electrically active impurities inactive and at the same time improve the homogeneity of the material.

Gallium arsenide plates as large as 7- by 14- by 0.6-inches were prepared by a unique "open" system. Several of these plates exhibited excellent physical and optical properties with measured MTF (Modulation Transfer Function) values as high as 98.7 percent. Many rain erosion samples, possessing similar properties, were cut from plates which contained some physical or optical defects.

The optimum compounding and growth system developed during the course of this program is basically a horizontal gradient freeze technique. However, ampuls normally used for this process are limited in size and geometrical configuration. To produce plates as large as 7 by 14 inches, it was necessary to (1) develop a process which did not rely on evacuated ampuls or (2) design a large ampul capable of being evacuated to a sufficiently low pressure. A computer

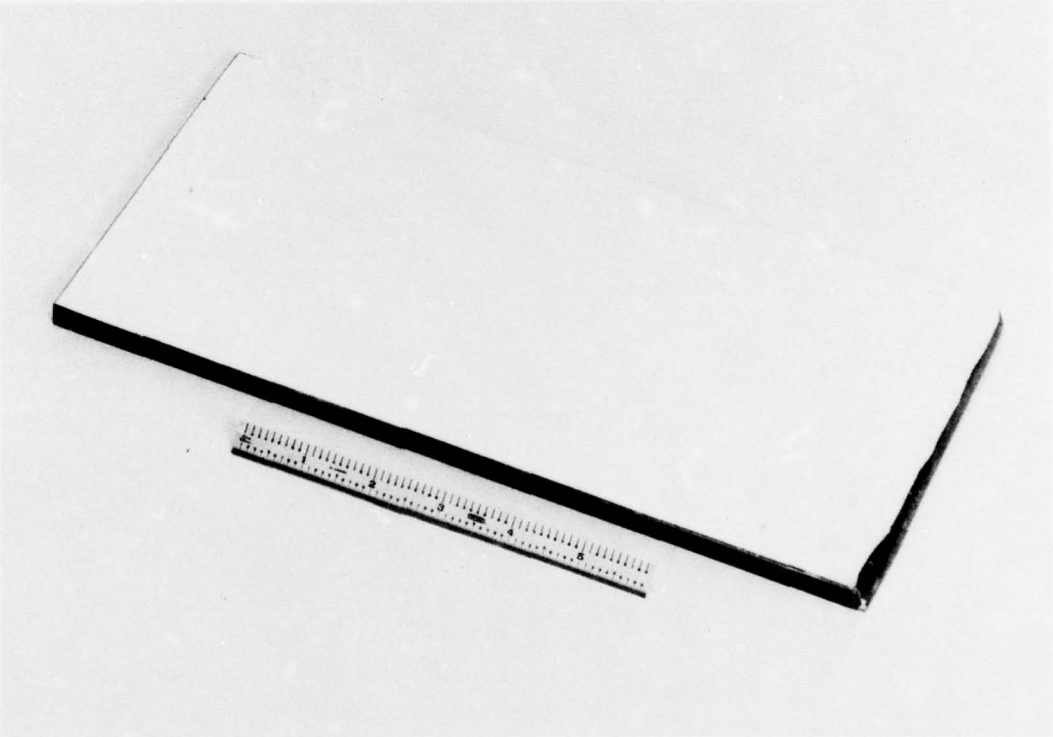


Figure 21. Photograph of 6 by 12 by 0.4 Inch Gallium Arsenide Polished Plate

analysis of the latter approach indicated that the thickness of the ampuls would have to be nearly 0.5 inch, assuming the ampul dimensions were 15 by 7 by 3 inches. This implies that larger ampuls would require even thicker walled quartz. Because of the difficulty in fabricating these ampuls, all efforts were directed toward developing the open system.

The process developed under this contract uses quartz ampuls with relatively thin wall thickness. These ampuls are not extremely difficult to fabricate nor do they require special quartz sizes and shapes. Ampuls as large as 14 by 22 inches have been fabricated using this technology. Figure 22 is a photograph of such an ampul. The existing Thermco furnace, in which the 6- by 12-inch plates were produced, is large enough to compound and grow plates up to 14 by 20 inches. However, scale-up to this size may present further unforeseen problems. The uniformity of dopants across a large solid-liquid interface is unknown. Also, the stability of large area quartz at these elevated temperatures may present some problems. Additional effort will most certainly be required to develop the optimum techniques for a production process.

Figure 22. Photograph of a 14 by 22 Inch Ampul

APPENDIX

ADVANCED ENGINEERING BRANCH
APPLIED MECHANICS SECTION
MEMORANDUM NO. 75-65-005
3 DECEMBER 1975

QUARTZ PRESSURE VESSEL
STATIC STRUCTURAL ANALYSIS
BY
JACK M. HARPER

I. SUMMARY

This report concerns the stress analysis performed on a quartz pressure vessel to determine the wall thickness required to give a maximum tensile stress of 1000 psi under a vacuum pressure distribution (14.7 psi). Two vessel configurations were analyzed. The first, a rectangular box with six flat sides produced a minimum wall thickness of 0.485 inch. The second vessel, which was like the first with the exception that the two largest sides were curved, produced a minimum wall thickness of 0.370 inch.

II. INTRODUCTION

The purpose of this analysis was to determine the wall thickness of a pressure vessel required to produce a maximum tensile stress of 1000 psi under a vacuum pressure distribution (14.7 psi). The vessel was to be made of quartz with the dimensions of 15 by 7 by 3 inches with an approximate thickness of 0.40 inch. All constants for quartz used in this analysis were obtained from General Electric Company and Amersil data sheets describing fused quartz. These constants are listed in Table A-1.

TABLE A-1. FUSED QUARTZ CONSTANTS

1.	Density	2.054×10^{-4} lb/in^3
2.	Poisson's Ratio	0.16
3.	Modulus of Elasticity	10.2×10^{6} lb/in^2
4.	Tensile Strength	6.96×10^{3} lb/in^2
5.	Design Tensile Strength	9.86×10^{2} lb/in^2

III. ANALYSIS

The finite element method and the Texas Instruments SAP IV structural dynamics computer program were employed. Due to symmetry of both models, only one-eighth of each had to be modeled. Both models consisted of 197 nodes and 171 plate elements. Results obtained from the two geometries are as follows.

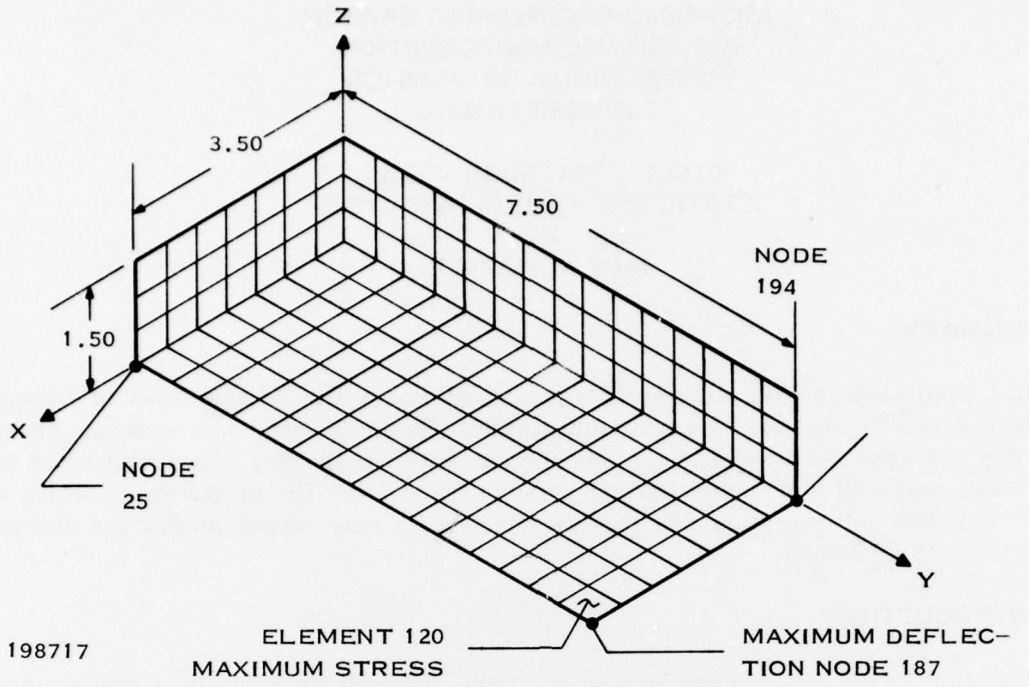


Figure A-1. SAP IV Model Rectangular Box With Flat Sides

A. Rectangular Vessel With Six Flat Sides

The model used for this analysis is shown in Figure A-1. Using an approximate thickness of 0.40 inch for all the sides, the analysis showed the maximum tensile stress on the model to be 1450 psi and to occur at element 120. This is higher than the recommended design tensile strength of 986 psi as stated by General Electric Company. Therefore, the thickness of the sides of the structure will have to be increased. Table A-2 shows a comparison of thickness versus tensile stress. Table A-2 also lists a margin of safety which is computed by the equation:

$$M_S = \frac{\sigma_D}{\sigma_C} - 1$$

where

σ_D = design tensile stress
= 9.86×10^2 lb/in^2

σ_C = calculated tensile stress.

Figure A-2 and Figure A-3 are plots of principal stress versus length from nodes 25 to 187 and nodes 194 to 187, respectively (see Figure A-1).

TABLE A-2. VARIATIONS OF MAXIMUM STRESS WITH THICKNESS FOR A FLAT-SIDED RECTANGULAR VESSEL

Thickness (*inch*)	Stress (lb/in^2)	Margin of Safety
0.4	1,450	−0.320
0.485	986	0.0
0.5	928	0.060
0.55	767	0.286
0.6	644	0.531
0.65	549	0.796
0.7	473	1.085
0.75	412	1.393

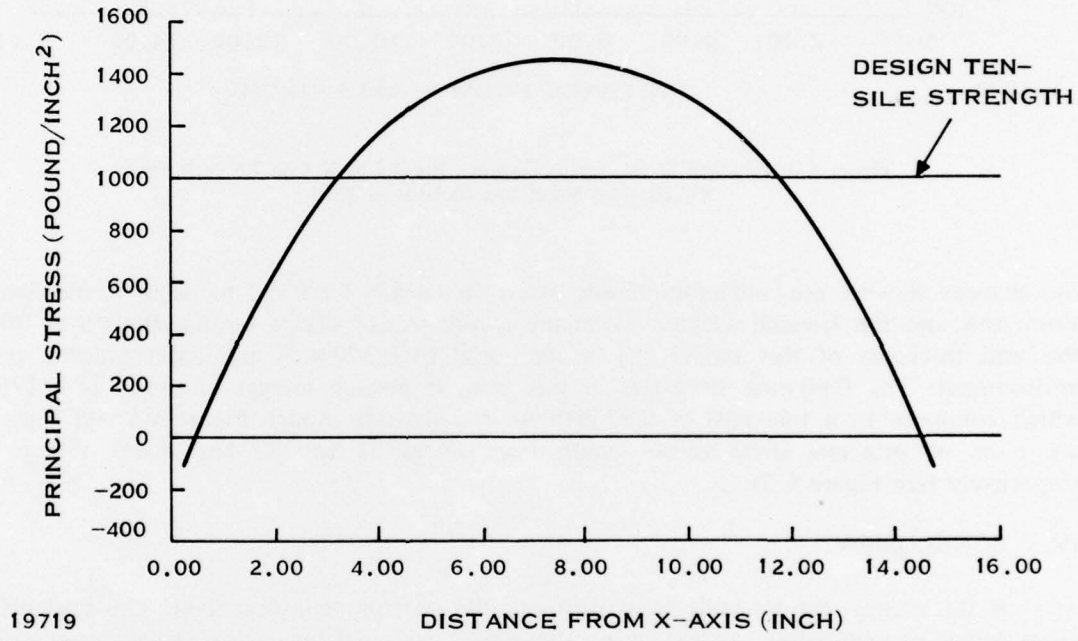


Figure A-2. Principal Stress Versus Distance Parallel to Y-Axis 3.5 Inch From Y-Axis Flat Sided Box (0.40 Inch Thick)

B. Rectangular Vessel with Four Flat Sides and Two Curved Sides

The model used for this analysis and its deflections are shown in Figure A-4. The model is identical to that used in the first analysis with the exception that the largest surface has a radius of curvature of 8.056 inch. Again using an approximate thickness of 0.40 inch for all the sides,

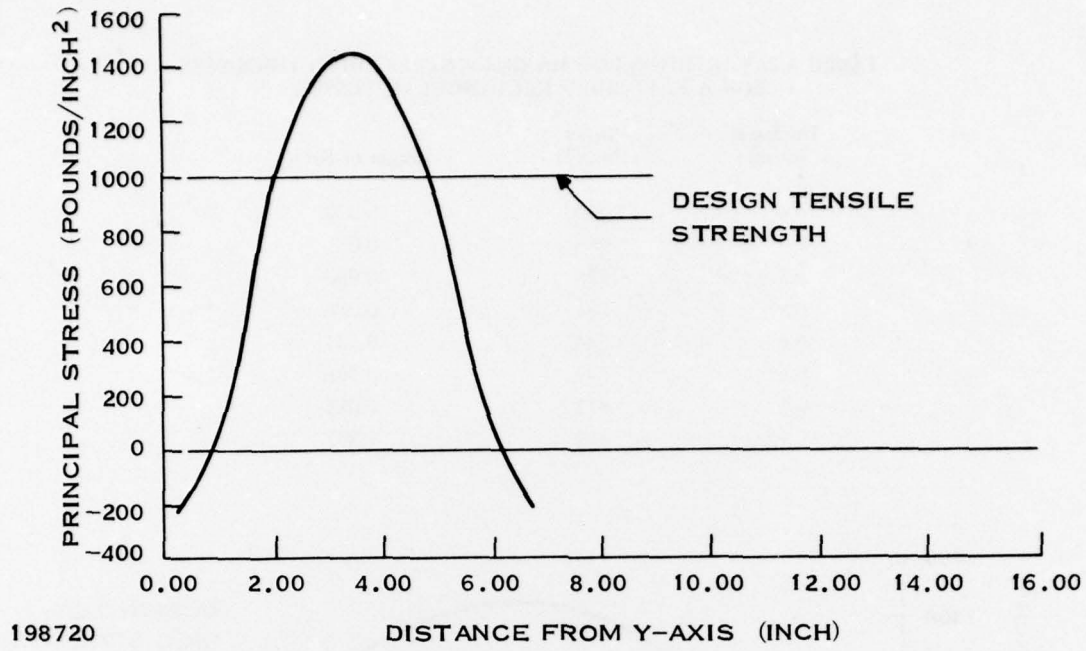


Figure A-3. Principal Stress Versus Distance Parallel to X-Axis 7.5 Inch From X-Axis–Flat Sided Box (0.40 Inch Thick)

the analysis showed the maximum tensile stress to be 839.1 psi and to occur at element 120. From this and the General Electric Company recommended design tensile strength of 986 psi, the wall thickness of this model can be decreased to 0.370 inch and withstand the vacuum environment. The 0.40 inch thickness in this analysis gives a margin of safety of 0.175 inch which compares to a thickness of 0.53 inch for the flat-side model. Figure A-5 and Figure A-6 are plots of principal stress versus length from nodes 25 to 187 and nodes 194 to 187, respectively (see Figure A-2).

IV. CONCLUSION

Both models can be built to perform in the environment described. The tradeoff that arises is cost of material versus cost of manufacture. In the instance of a six-sided vessel with flat sides, the thickness of the walls will have to be 0.485 inch as opposed to 0.370 inch for the vessel with two curved sides for the tensile stress not to exceed 1000 psi. In the instance of the six-sided vessel with the 15- by 7-inch sides curved, curved sheets of quartz will have to be dealt with These tradeoffs should be investigated prior to a decision.

Another factor that may influence the decision is deflection. The flat sided model had a maximum deflection of 0.00291 inch while the model with curved surfaces deflected 0.00186 inch. This showed an increase of 56 percent in deflection of the flat sides over the curved sides.

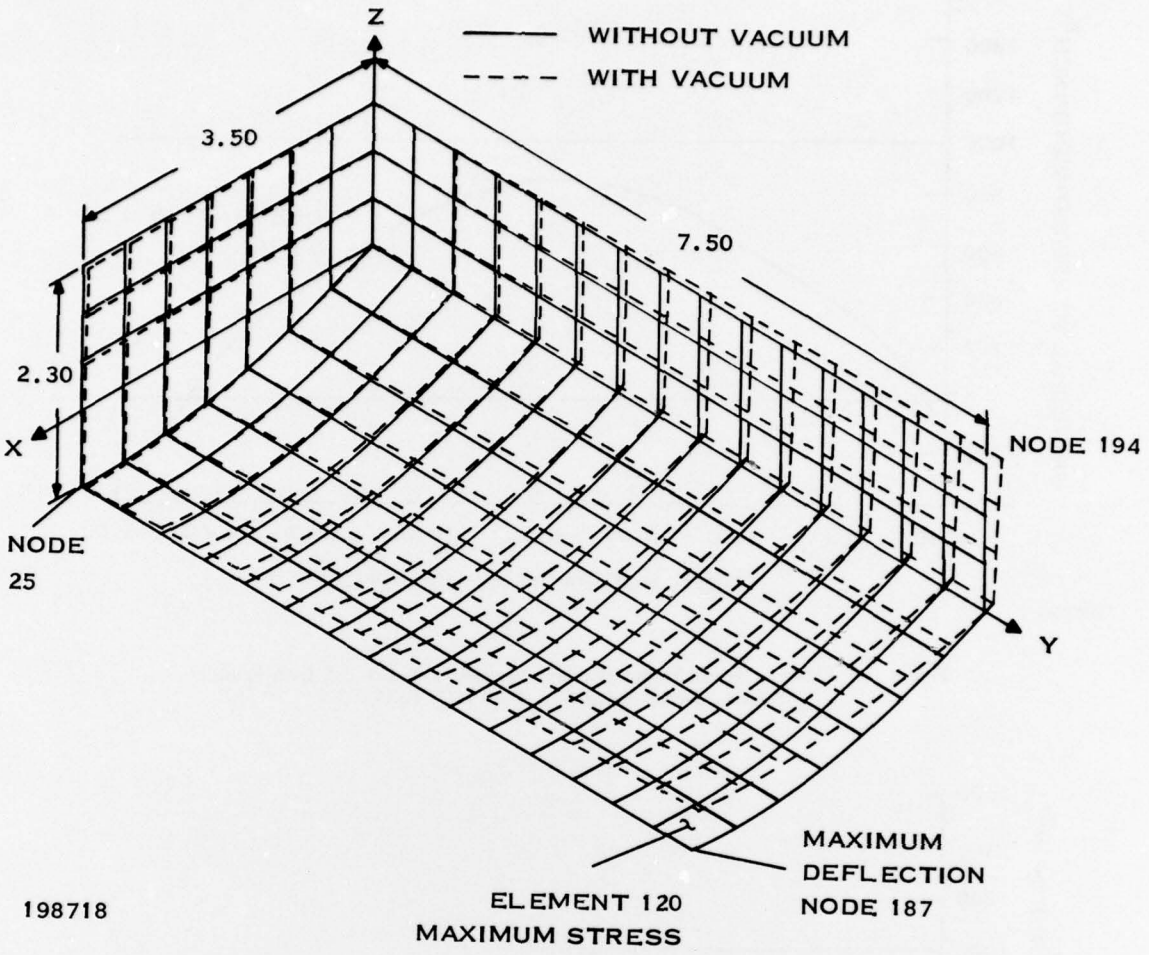


Figure A-4. Deflection of Six-Sided Box With Two Curved Surfaces

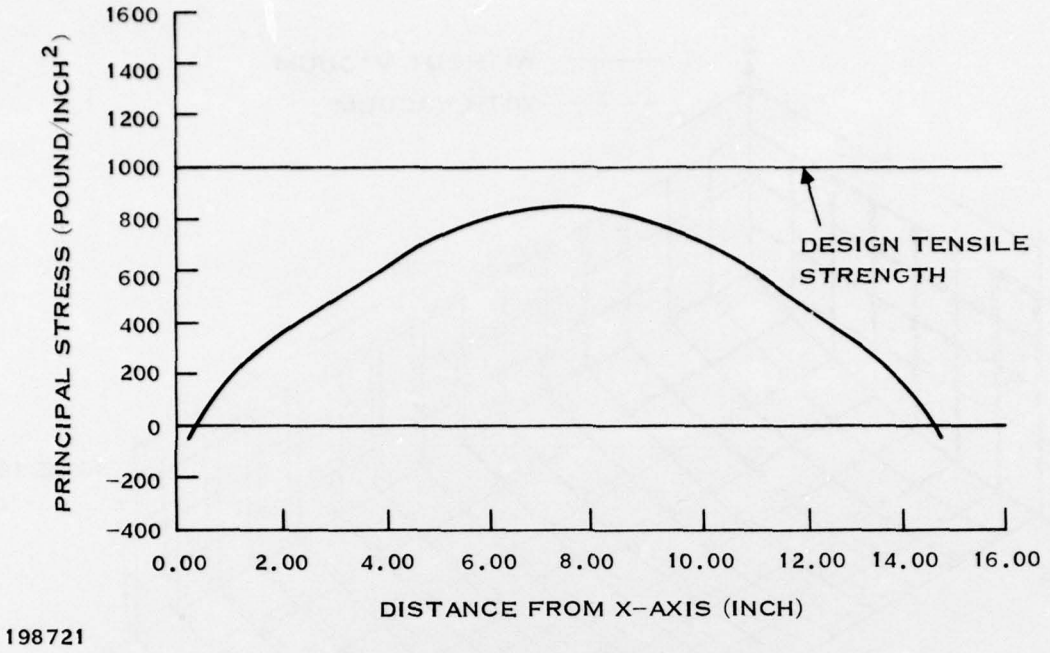


Figure A-5. Principal Stress Versus Distance Parallel to Y-Axis 3.5 Inch From Y-Axis—Curved Sided Box (0.40 Inch Thick)

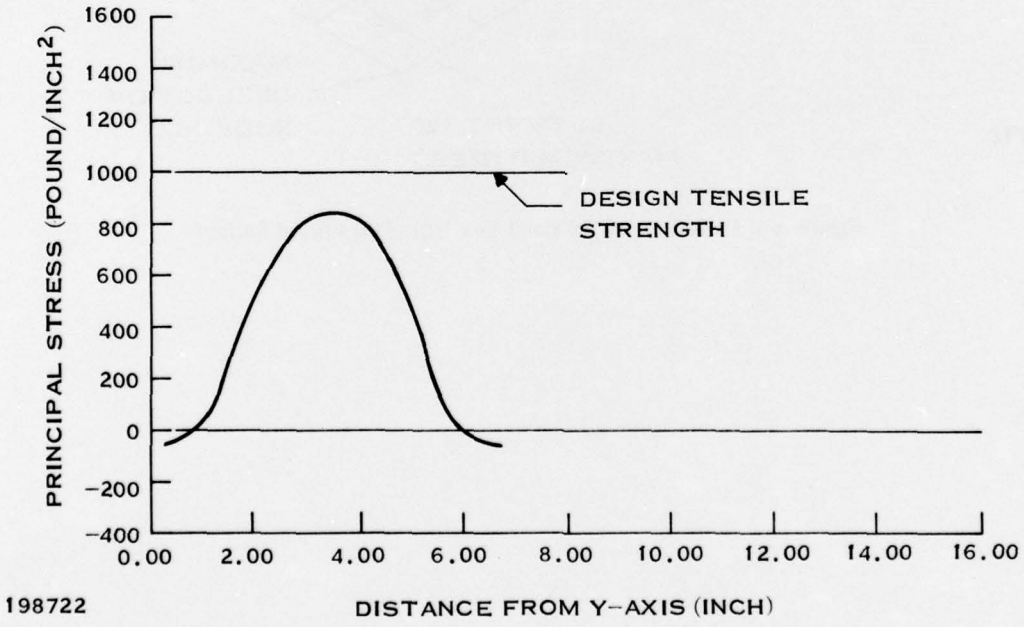


Figure A-6. Principal Stress Versus Distance Parallel to X-Axis 7.5 Inch From X-Axis—Curved Sided Box (0.40 Inch Thick)

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