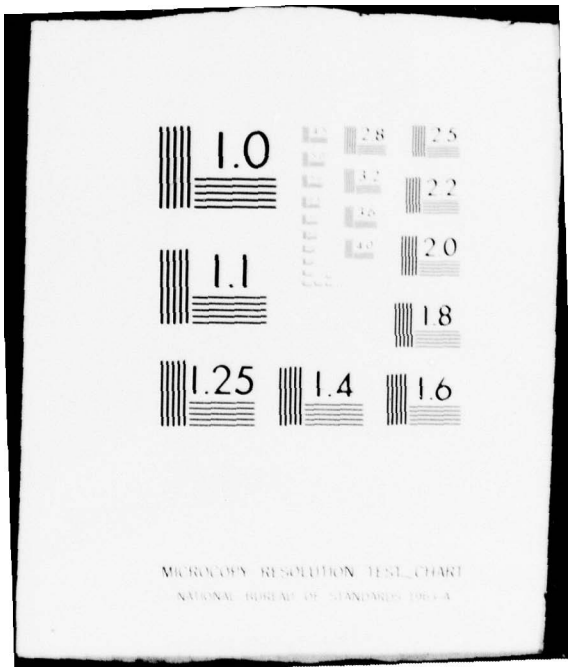
AD-A070 280 CRYSTAL SPECIALTIES INC MONROVIA CA F/G 20/2
STUDY CZOCHRALSKI LIQUID-SEAL CRYSTAL GROWING TECHNIQUE.(U)
APR 79 J K KENNEDY, W P ALLRED F19628-76-C-0118
UNCLASSIFIED RADC-TR-79-86 NL

| OF |
AD
A070280

END
DATE
FILMED
7-79
DDC


1.0
1.1
1.25
1.4
1.6
2.0
1.8
2.2
2.5
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

LEVEL II

RADC-TR-79-86
Final Technical Report
April 1979

STUDY CZOCHRALSKI LIQUID-SEAL CRYSTAL GROWING TECHNIQUE

Crystal Specialties, Inc.

John K. Kennedy
Worth P. Allred

ROME AIR DEVELOPMENT CENTER
Air Force Systems Command
Griffiss Air Force Base, New York 13441

This report has been reviewed by the RADC Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

RADC-TR-79-86 has been reviewed and is approved for publication.

APPROVED: John K Kennedy

JOHN K. KENNEDY
Project Engineer

APPROVED:

ROBERT M. BARRETT
Director, Solid State Sciences Division

FOR THE COMMANDER: John P. Huss

JOHN P. HUSS
Acting Chief, Plans Office

If your address has changed or if you wish to be removed from the RADC mailing list, or if the addressee is no longer employed by your organization, please notify RADC (ESM), Hanscom AFB MA 01730.

Do not return this copy. Retain or destroy.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: RADC-TR-79-86	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): STUDY CZOCHRALSKI LIQUID-SEAL CRYSTAL GROWING TECHNIQUE	5. TYPE OF REPORT & PERIOD COVERED: Final Technical Report
	6. PERFORMING ORG. REPORT NUMBER: N/A
7. AUTHOR(s): John K. Kennedy Worth P. Allred	8. CONTRACT OR GRANT NUMBER(s): F19628-76-C-0118
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Crystal Specialties, Inc. 419 W. Maple Avenue Monrovia CA 91016	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61101F ILIR6CAA
11. CONTROLLING OFFICE NAME AND ADDRESS: Deputy for Electronic Technology (RADC/ESM) Hanscom AFB MA 01730	12. REPORT DATE: April 1979 13. NUMBER OF PAGES: 28
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): Same	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: N/A

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)

Same

18. SUPPLEMENTARY NOTES

RADC Project Engineer: John K. Kennedy (ESM)

This research was supported by the Air Force In-House Laboratory Independent Research Fund

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

Czochralski Liquid-Seal Growing Technique	thermal fracture	(Cont'd)
Horizontal Bridgman Technique	fused quartz	
resistance furnace	boron nitride	
direct RF coupling	vitreous carbon	
kanthal wire furnace	growth and arsenic chambers	

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

N-Type, P-Type and semi-insulating (Chrome dope) single crystals of Gallium Arsenide were grown using the Czochralski Liquid-Seal Technique.

Boron Nitride was selected as the crucible material that would yield the best quality single crystals.

Single Gallium Arsenide crystals of up to 300 grams were grown as a result of modifications made in the puller apparatus.

Experiments were conducted to identify the cause of impurity contamination →

DD FORM 1 JAN 73 1473

UNCLASSIFIED 392219

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Item 19 (Cont'd)

quartz pull rod
coron oxide (B_2O_3), B_2O_3 acts as a "getter", thermal conversion
N-Type
P-Type
semi-insulating Gallium arsenide single crystals
thermal gradients
silicon contamination via breakdown of quartz
necking down crystals to remove dislocations
gallium arsenide melt
stoichiometry
orientation
Van DerPauw Data (Hall Data)
carrier concentration
mobility
resistivity

Item 20 (Cont'd)

during the growth process. The results of these experiments indicated that:

1) The introduction of Boron Oxide (B_2O_3) to the Gallium Arsenide melt absorbed impurities.

2) Silicon (si) was being introduced to the melt by the breakdown of the quartz ($2SiO_2 \quad 2SiO+O_2$). This was caused by the natural gas-oxygen torch, which heats the quartz chamber to prevent Gallium Arsenide condensation.

3) A special viewport, heated by a resistance furnace rather than a natural gas-oxygen torch was used to reduce silicon contaminants. As a result of this experiment, an undoped semi-insulating crystal of extremely high purity was grown.

SUMMARY

A study utilizing the Czochralski Liquid-Seal Crystal Growing technique was undertaken to grow doped and undoped single crystals of gallium arsenide (GaAs). Tests for high purity using various crucible materials i.e. boron nitride, vitreous carbon, fused quartz, aluminum oxide, and aluminum nitride were conducted with the liquid-seal Czochralski apparatus.

After evaluation, boron nitride was selected as the crucible material that would yield the best quality single crystals. N-type, p-type, and semi-insulating (Cr-doped) gallium arsenide crystals of 50 to 150 grams were then grown using the boron nitride crucibles.

The liquid-seal Czochralski puller was then modified to permit large diameter crystals of 150 to 300 grams to be grown. Large diamter n-type, p-type and semi-insulating single crystals were grown in the modified puller.

Further experiments were conducted to identify the cause of impurity contamination during the growth process. From these results, modifications were made in the growing techniques and equipment. The results of these experiments indicated that:

1) The introduction of boron oxide (B_2O_3) on the GaAs melt absorbed impurities from the melt.

2) Si was being introduced to the melt by the breakdown of the quartz ($2SiO_2 \longrightarrow 2SiO + O_2$). This was caused by the natural gas-oxygen torch, which heats the quartz chamber to prevent GaAs condensation.

3). A special viewport, heated by a resistance furnace rather than a natural gas-oxygen torch, was used to reduce silicon contaminants. As a result of this experiment an undoped, semi-insulating crystal was grown. Preliminary measurements at Hughes Research Center indicates this material to be of extremely high purity.

TABLE OF CONTENTS

EVALUATION

1. This report is the Final Report on the contract. It covers research done on the growth of gallium arsenide single crystals during the period 30 December 1975 through 30 June 1978. The objective of this research was an evaluation of the liquid seal Czochralski crystal growth system for the growth of high purity gallium arsenide useful for electrooptic application. A liquid seal Czochralski growth system was built and then modified to grow 150-300 gram gallium arsenide crystals. High purity undoped (semi-insulating) and intentionally doped crystals were grown using this system.

2. The above work is of value since it provides basic knowledge and a new crystal growth technique for the growth of high purity gallium arsenide crystals for use as substrates for electrooptic applications.

John K. Kennedy

JOHN K. KENNEDY
Project Engineer

1.0 LIST OF ILLUSTRATIONS

2.0 LIST OF TABLES

3.0 OBJECTIVE

3.1 - The objective of this contract was to develop a method for the growth of single GaAs crystals with properties superior to those found in crystals grown by the methods in current use.

High purity GaAs is needed in the growth of microwave epitaxial layers. One of the severe problems encountered is that of conversion.

Semi-insulating GaAs substrate material which measures 1×10^8 ohm-cm prior to heat treating, usually converts on the surface to a lower resistivity. The effect is a conducting path beneath the epitaxial grown layer which deteriorates the device parameters. The reason for the conversion is not fully understood, but it is thought to be associated with the impurities currently found in grown crystals.

"Thermal conversion" of the substrate is one of the major problems still degrading the device performance. Several mechanisms have been proposed to explain the conversion mechanism. However, to date, no model has been proposed that would help the crystal grower to eliminate this problem. It appears however, that silicon is one of the major contributors to this problem.

3.2 Czochralski growth of gallium arsenide has presented some problems primarily because of the volatility of arsenic. The arsenic vapor pressure at the melting point is about one atmosphere. A vapor space over the melt can permit transport of arsenic and condensation of solid arsenic on any cool portions of a sealed system. Condensation may be avoided by maintaining the entire enclosure at a temperature such that the vapor pressure of pure arsenic is greater than the arsenic partial pressure over the melt. Since the temperature needed to provide a stoichiometric pressure is 610°C, a problem arises in providing a seal for the pulling mechanism which will withstand this temperature. A second problem is the higher reactivity of the arsenic vapor with many materials at 600°C.

Several methods have been employed previously to avoid loss of arsenic from the melt. The earliest technique is the magnetic-type puller developed by Gremmelmaier.[1] This method uses magnets to support and rotate the seed rod which is sealed within the quartz chamber. Since there is no mechanical feed through, the temperature of the entire quartz envelope can be heated to a temperature in excess of 610°C. One of the major disadvantages of the magnets, is that it is subject to considerable vibration. This problem is caused by the loose coupling of the magnet and by the friction of the quartz bearing surfaces. In addition, the system is very complex, costly, and difficult to use.

A second method uses a liquid gallium seal to contain the arsenic vapor.[2] However, it proved to have little practical use because of its complexity and the fact that the arsenic in the growth chamber reacts with the gallium seal to form solid gallium arsenide. Arsenic is also lost through the gallium seal.

The third method is the liquid encapsulation technique.[3,4] This systems uses a layer of molten B_2O_3 on the surface of the GaAs melt to prevent the escape of arsenic. The B_2O_3 enables the use of conventional Ge or Si growers for the growth of GaAs. The growing crystal is pulled through the B_2O_3 layer. A layer of B_2O_3 adheres to the crystal and generates stresses as it cools due to the differences in thermal expansion. It is also difficult to react elemental gallium and arsenic under the B_2O_3 layer, making it necessary to use pre-reacted GaAs for the starting material. One of the major problems inherent with the liquid encapsulation technique is that of O_2 contamination arising from the B_2O_3 directly in contact with the melt.

The method of growth predominantly used at Crystal Specialties, Inc. to grow single GaAs crystals is the horizontal Bridgman technique. This method is similar to the gradient-freeze technique in that they both produce single crystals in hot quartz ampoules. This leads to Si contamination of the GaAs melt. The two methods differ only in that solidification by the gradient-freeze technique takes place by the movement

of a temperature gradient along the ingot, making the entire system stationary. The horizontal Bridgman method requires the movement of either the furnace (as is done at Crystal Specialties, Inc.) or the ampoule, housing the ingot.

The main advantage of horizontal growth is that crystals can be grown automatically with little supervision. The critical factor in either procedure is the interaction between the boat and the melt, since this can seriously affect the final crystallinity. The most desirable material used for boats is fused quartz. The disadvantage in using quartz is of Si contamination. The quartz wall in these systems reach 1250°C. This causes a breakdown of SiO_2($2SiO_2 \longrightarrow 2SiO + O_2$). As a result, Si contamination of about 1×10^{16} impurities/cm^3 is introduced into the GaAs melt.

3.3 - As an answer to the above mentioned problems, the liquid-seal growth technique was elected. The system uses a molten B_2O_3 seal, not in contact with the melt, to prevent arsenic escape. The liquid-seal technique was thought to have an advantage over both systems in that it would have a cooler quartz wall coupled with no B_2O_3 in contact with the molten GaAs.

4.0 - APPROACH

4.1 - In addition to the advantage over the horizontal growth methods, because the temperature of the quartz walls remains below 700°C, the liquid-seal system also has an advantage over the magnetic type grower in that it does not use magnets to effect the vertical displacement and rotation of the seed crystal. Since a direct mechanical drive is used, the smoothness of the rotation and pull is limited only by the mechanical system. This grower is also thought to have advantages over the liquid encapsulated Czochralski Technique in that pre-reacted material is not necessary, because gallium and arsenic can be reacted directly in the system. In addition, the problem of B_2O_3 adhering to the crystal is eliminated.

With the liquid seal drive system, there is no difficulty in necking down the seed to a diameter of 1-2mm before enlarging the diameter of the crystal. Using this necking down procedure single crystals with dislocation densities below 100 pits/cm^2 can be grown.

The liquid seal Czochralski system was also modified at Crystal Specialties, such that it could grow large diameter semi-insulating GaAs. The large capacity is needed so that research labs evaluating this material will have wafers with larger areas than was possible with the original system.

4.2 - The liquid seal technique is also a desirable method for evaluating various crucible materials. This is possible since crystals can be grown with no B_2O_3 in contact with either the crucible or GaAs melt and the fact that minimal Si is introduced from the quartz wall. Therefore, GaAs can be reacted in various crucibles to determine which crucible will yield the purest crystals.

A technique similar to the liquid seal has been developed but using the principle of pressure balancing.[5] In this system, the disassociation pressure of the compound is dynamically balanced by a pressure of inert gas. The liquid seal technique presented here differs, in that it does not attempt to balance the differential pressure. It utilizes the fact that the B_2O_3 is extremely viscous at 650°C. The liquid B_2O_3 seal remains in position during the entire crystal growth process and prevents the leakage of arsenic from the growth chamber. The complex pressure balancing apparatus is therefore unnecessary for the growth of GaAs. The liquid seal technique is, therefore, much simpler than the pressure balancing technique.

The most attractive feature of the liquid seal technique is its simplicity. It is economical to construct, easy to load and keep clean.

5.0 - EXPERIMENTAL

5.1 - The growth system consists of:

1. A 15 KW, 240V Radio Frequency (RF) Generator
2. Turbo vacuum pump system.
3. Czochralski crystal grower
4. Data trak control console for item 3.

5.2 - The following procedure has been the most successful for pulling single GaAs crystals, using the liquid seal technique.

The first step involves the complete cleaning of all materials that would come

in contact with the gallium (Ga) and arsenic (As) during growth. Materials such as the quartz chamber, rod and stand, and the crucibles, (boron nitride, aluminum nitride, vitreous carbon, aluminum oxide or quartz) fig. 1, are cleaned and etched thoroughly using a 1:1 mixture of nitric and hydrochloric acid for 30 minutes. The crucibles used were flat bottom style crucibles. The approximate size was 25mm deep x 50mm wide, with a 1.0mm wall thickness. All the crucibles were supported by a quartz stand. The boron nitride (BN) crucible used for the larger diameter crystals of up to 300 grams was 60mm wide and 40mm deep, with a 1.0mm wall thickness. A stoichiometric amount of gallium and arsenic is then loaded into the chamber, which is then sealed to the top section, by welding with quartz. An additional amount of As is added to provide an As vapor pressure above the melt. A 2.0 gram pellet of B_2O_3 is placed in the upper chamber and the entire chamber is then loaded into the resistance furnace. The resistance furnace is used to maintain proper temperatures for different regions of the growth system during growth. This furnace was modified from a single to a split furnace to provide greater efficiency in chamber installation, with less danger of damage to the chamber.

The vacuum system is then turned on, and the nitrogen trap filled to remove impurities from the pump. Helium pressure to the system is set at 6-8 PSI. The entire chamber is repeatedly flushed with high purity helium, then outgased to remove residual O_2 and other gases. During the outgasing, the main chamber and As chamber (Fig. 1) are heated with a hand held gas-oxygen torch, to help drive off any moisture or oxides.

While the entire chamber is being outgased, the top furnace is set at 900°C to melt the 2.0 grams of B_2O_3 down into the neck of the chamber. The molten B_2O_3 provides a seal for the bottom chamber. The bottom furnace is then heated to 300°C.

An RF coil is then placed around the bottom chamber to heat treat the gallium. The entire chamber is backfilled with helium and outgased several times during heat

treatment. The heat treatment process lasts approximately 2 hours.

After heat treatment, the entire chamber is pumped down to a vacuum of 2×10^{-5} Torr, via a side port, then backfilled with 2 PSI of helium. The quartz vacuum port connected to the bottom chamber is then sealed off via the gas-oxygen torch. (See Fig. 1).

The top furnace control is then dropped to 650°C. While the temperature is decreasing, the helium pressure is increased to 1.0 atmosphere positive pressure in the upper chamber to drive the B_2O_3 between the pull rod and the neck of the pull chamber. Due to the high viscosity of the B_2O_3 at 650°C, the differential pressure between the helium filled section and the growth chamber is not critical. When the B_2O_3 has filled about 2/3 of the length of the space between the rod and the tube, the seal for the growth chamber is complete. This enables the B_2O_3 to form a viscous tight seal and allows the 5mm seed rod to be able to rotate and move up and down as needed. The pull rod rotates through the liquid seal so that a direct mechanical drive similar to that used in conventional Ge or Si growers can be used.

The As is then driven from the As chamber into the growth chamber, using the hand held natural gas-oxygen torch. The As chamber is then sealed off via the torch.

The RF coil used to provide energy for the reaction, couples directly to the Ga and As melt. Thus, only the GaAs and the crucibles are heated to the melting point of GaAs. By coupling directly to the melt, the wall of the growth chamber in which the crystal is grown can be held at a relatively low temperature, approximately 700°C.

5.3 - Reaction of the Ga and As then commences by heating the gallium to 1060°C. A natural gas-oxygen flame is placed in the front portion of the growth chamber. The heat from this torch prevents condensation of GaAs which is evaporated from the surface of the GaAs melt on a window used to visually inspect reaction and growth. During reaction, the bottom furnace temperature is gradually increased to drive the As into the Ga. After approximately 2-3 hours, reaction is completed and single crystal growth is ready to begin. Seeding is accomplished by lowering the seed, which

is fastened to the bottom of the quartz pull rod with tantalum wire, into contact with the melt. Growth is then initiated by raising the seed. The pull rate is approximately 1/2 " per hour and the seed rotation 12 RPM.

To remove dislocations at the start of growth, the crystal is necked down from the seed diameter, to approximately 3mm in diameter, then grown out to the desired width. As growth progresses, the temperature is progressively lowered to maintain a constant diameter. After the crystal is grown, the furnaces are allowed to cool, after shut down. The differences in thermal expansion of the B_2O_3 and the quartz causes the pull rod and the surrounding quartz tubing to fracture. This necessitates replacement of the quartz pull rod and the surrounding tubing for each crystal grown.

6.0 - RESULTS

Single crystals of GaAs have been grown by the liquid seal technique. The first phase of the study tested the liquid seal technique as a method for production of high purity crystals. In addition, various crucible materials for growth of the highest purity GaAs was tested.

6.1 - Table #1 is a summary of crystals grown to test the purity of various crucible materials.

The crucibles grown from fused quartz crucibles, no. 12 and 20 were found as expected to be contaminated with silicon, resulting in low resistivity. This is the result of the hot Ga reducing the SiO_2 during reaction and growth. This was anticipated as this effect has been observed when crystals were grown in quartz by other techniques.

Crystals 21 and 22, grown from aluminum oxide crucibles, were single crystals. However, a high incidence of failure was experienced in pulling from AL_2O_3 crucibles because of thermal fracture of the crucible during reaction.

Growth was done by coupling directly to the GaAs melt with RF induction heating. Direct RF coupling to the melt gives ideal condition for crystalline purity. However, due to steep thermal gradients crystalline perfection is sacrificed. Using a vitreous

carbon susceptor, to hold a boron nitride crucible, would improve thermal gradients. However, this crucible gives very little temperature gradient across the melt surface, causing crystals to nucleate at the crucible and grow in from the side. As the diameter of the growing crystal is increased, the nucleated crystal interferes with the growing crystal. This was the case in crystals #24 and 25. There also appeared a scum-like deposit on the melt surface which is probably carbon coming from the carbon material.

Crucibles of aluminum nitride have been the most difficult to use. They tend to fracture during growth, and only one crystal has been successfully grown from aluminum nitride. It is felt for this reason that aluminum nitride is not suitable for GaAs crystal growth.

6.2 - The undoped crystals grown in pyrolytic boron nitride (PBN) crucibles (#2, 5 and 8) were more easily grown. This fact, plus the high purity of the crucible and the compatibility of its constituents, boron and nitrogen, with GaAs, makes boron nitride a very good material for GaAs crystal growth. Also, the crucible is capable of being used a number of times, which enhances its value in a production process.

After boron nitride was chosen the purest and best suited crucible material, the remaining two n-type, two p-type, and two semi-insulating (Cr-doped) crystals were grown in boron nitride crucibles.

6.3 - Undoped single crystal grown in high purity PBN crucibles proved a donor (n-type) concentration of approximately $5.0 \times 10^{16}/cm^3$. In an attempt to determine the source of this level of contamination, several modifications were made. They were:

1. Complete overhaul and cleaning of all gas and vacuum lines in the crystal grower and vacuum pump system.
2. Replacement of tantalum wire to hold the seed to the rod, with an all quartz seed holder.
3. Outgasing the chamber using high purity Helium.
4. Heat treating the gallium before reacting with arsenic.
5. High purity, low temperature sealing glass.
6. Gas purge while welding the bottom chamber closed.

7. Evaluating material produced by reacting in the bottom chamber, while the top chamber was sealed off.

8. Evacuate chamber on the pump used for horizontal Bridgman ampoules.

9. Use of an isolated arsenic chamber.

In spite of the above mentioned variations in techniques and system modifications, no variation in carrier concentration was noted. (Table #2, #47).

6.4 - It has been reported that B_2O_3 in contact with GaAs melt absorbs impurities such as Si from the melt. To test this idea, a small amount of B_2O_3 was added to the gallium prior to reacting with arsenic. Care was taken to add only enough B_2O_3 to cover the edges of the melt so that reaction of the arsenic with the gallium would not be blocked.

The amount of B_2O_3 per experiment varied from 1.0 to 7.0 grams. The B_2O_3 always formed a ring around the inside of the crucible on the surface, after the As reacted with the Ga. If a thin film of B_2O_3 completely covered the melt, it was driven to the sides of the crucible during reaction. A pellet of 12.0 grams of B_2O_3 was used in one run and it covered the entire top of the gallium surface, preventing arsenic from reacting with the gallium.

Before high purity crystals were pulled using B_2O_3 in the melt, tests were done that involved reaction of Ga and As, but with no pulling (Fig. 2, Table 2-51, 52). This was done to eliminate the possiblity that the 5.0×10^{16} n-type impurity was originating from the vacuum lines or the upper pull section.

The bottom chamber was sealed at the joint with the small I.D. tube. The chamber was evacuated on the pump used for horizontal Bridgman ampoules. Thus, the pull section and vacuum lines were removed as possible contaminating sources. The heat treating and reaction was performed in the same manner as previously described. After all the arsenic was reacted with the gallium, the temperature of the GaAs was slowly lowered below its freezing point. By this method, single crystals were grown on the surface of the melt for evaluation. After initial results indicated material produced in this manner resulted in no higher purity (Fig 2, Table 2 - 47), crystals were

pulled with the B_2O_3 in the GaAs melt. The variance in amounts of B_2O_3 used, did not seem to affect the crystal purity. It appears that B_2O_3 acts as a "getter" for impurities. These undoped crystals grown with B_2O_3 on the melt, resulted in material that was semi-insulating. (Fig. 2, Table 2 - 58,60). From this experiment it appears that B_2O_3 acts as a "Getter", and is also contributing O_2 as a compensating impurity.

The source of the n-type impurity in the GaAs was still unknown. It was suggested by Dr. John Kennedy of AFCRL, that the quartz heated by the natural gas-oxygen torch to provide a window might heat the quartz to a sufficient temperature to cause disassociation of the quartz and result in a contamination of Si.

Silicon is incorporated into the melt via breakdown of the quartz chamber.

$$(1)\quad 2SiO_2 \longrightarrow 2SiO + O_2$$

Contamination exists due to the volitile nature of SiO.

$$(2)\quad 3SiO + 2Ga \longrightarrow Ga_2O_3 + 3Si \text{ (in melt)}$$

6.5 - Material was therefore compounded by the technique described where no seed was used to produce test material. (Fig. 2). In this case however, no gas torch was used. As was expected the window area was clouded over shortly after reaction was started. After reaction, single crystals were again grown on the surface of the melt by slow cooling. This melt also contained B_2O_3 as a "getter". Van der Pauw measurements made on this material (#78 - Table 2) showed a marked decrease in carrier concentration, and an increase in mobility and resistivity.

Material was then grown with a special viewport, using a variac controlled resistance furnace (Fig. 3). The kanthal wire furnace enveloped the viewport and was insulated with asbestos cloth. The furnace was turned on when the As was being driven into the main chamber and left on thru the entire run. The variac was adjusted to maintain a temperature high enough to keep the viewport clear of As and oxides and low enough to prevent disassociation of the quartz, which would result in a SiO contaminant in the melt. There was greater difficulty in viewing the seeded

area of the melt, due to the 3" length of the viewport. A possible alternative to improve visibility, would be a shorter and wider viewport. Results of this test, evaluated by Hughes Research Labs (Table 1 #80), indicated extremely good semi-insulating material.

6.6 - Large diameter crystals delivered to Hanscom Air Force Base, were: two n-type, two p-type, two semi-insulating, Cr-doped.

Enclosed in Table 2 is Van der Pauw data, at room temperature, obtained at Crystal Specialties for the large diameter single crystals.

All of the crystals grown were on a (111) orientation, with the arsenic face contacting the GaAs charge. All of these crystals were grown in boron nitride curcibles since boron nitride provided the best purity of the crucible materials evaluated.

Difficulty occured in growing large diameter crystals, due to the uneven heating as the growth level lowered inside the crucible. As the crystal width increased greater than 1.0" and the growth level lowered, the growth temperature became very critical and erratic. At this point is was difficult to maintain a constant diameter and good single crystal growth conditions.

CONCLUSION AND RECOMMENDATIONS

(1) Pyrolytic boron nitride crucibles are the most desirable for growing high purity GaAs crystals. This is due to the compatibility of the boron and nitrogen from the crucible with the GaAs, and its mechanical stability and high purity. Boron nitride is also an economical material to use, because it can be used repeatedly.

(2) B_2O_3 in direct contact with the GaAs melt, seems to draw impurities from the melt by acting as a "getter" for the impurities.

(3) Si contamination observed in the original crystals was found to be produced by the high temperature window. This Si contamination was reduced by replacing the gas-oxygen torch on the growth chamber, with a resistance furnace, to provide a viewport to the growing crystal.

As a result of Run #80 where a carrier concentration of $4.0 \times 10^{10}/cm^3$, mobility of $5400 cm^2$/volt-sec and resistivity of 10^7 ohm-cm was obtained, Hughes Research Laboratories is very interested in obtaining material of this quality for Liquid-Phase Epitaxial source material.

Results from this research on undoped GaAs indicates that high purity material needed for source materials can be grown by this method. Results also indicate that further research in systems of this type is warranted. Additional research is also needed to determine the effects of not using B_2O_3 on the GaAs melt, in conjunction with the addition of the resistance furnace viewport.

FISCAL STATEMENT

Of the total funds of $82,261.00 authorized for both phases of the contract, approximately 98% has been expended. This last figure (98%) includes 85% of the allowable fee. All of the work has been completed except for the Final Report.

COST DATA

Cumulative cost data as of 30 October 1978.

Labor Elements	Planned		Actual	
	Labors Hrs.	Amount	Labor Hrs.	Amount
Sr. Scientist	750	$8025.00	1568.5	$16,092.78
Jr. Scientist	2400	15064.00	2256.25	11,075.07
Other Expenses				
Purchased Parts		17888.00		10,387.75
Raw Material		12606.00		14,680.85
Total Other Expenses		30494.00		25,068.59
Overhead		18963.00		23,025.00
Travel		1200.00		-
Preparation of Reports		2000.00		-
G & A		1515.00		1,505.22
Grand Total		$77261.00		$76,766.66

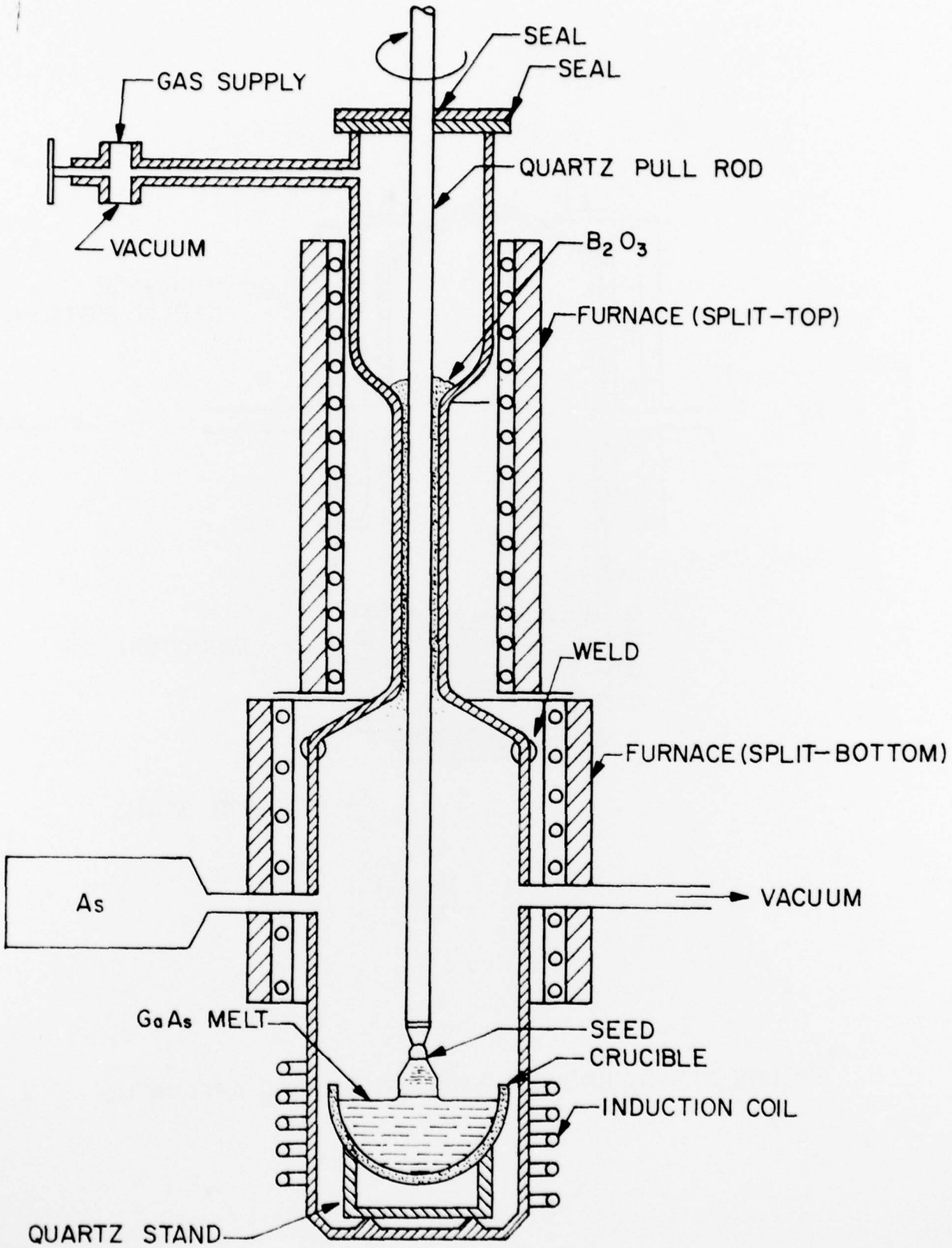


FIGURE 1. LIQUID-SEAL CZOCHRALSKY GaAs GROWER

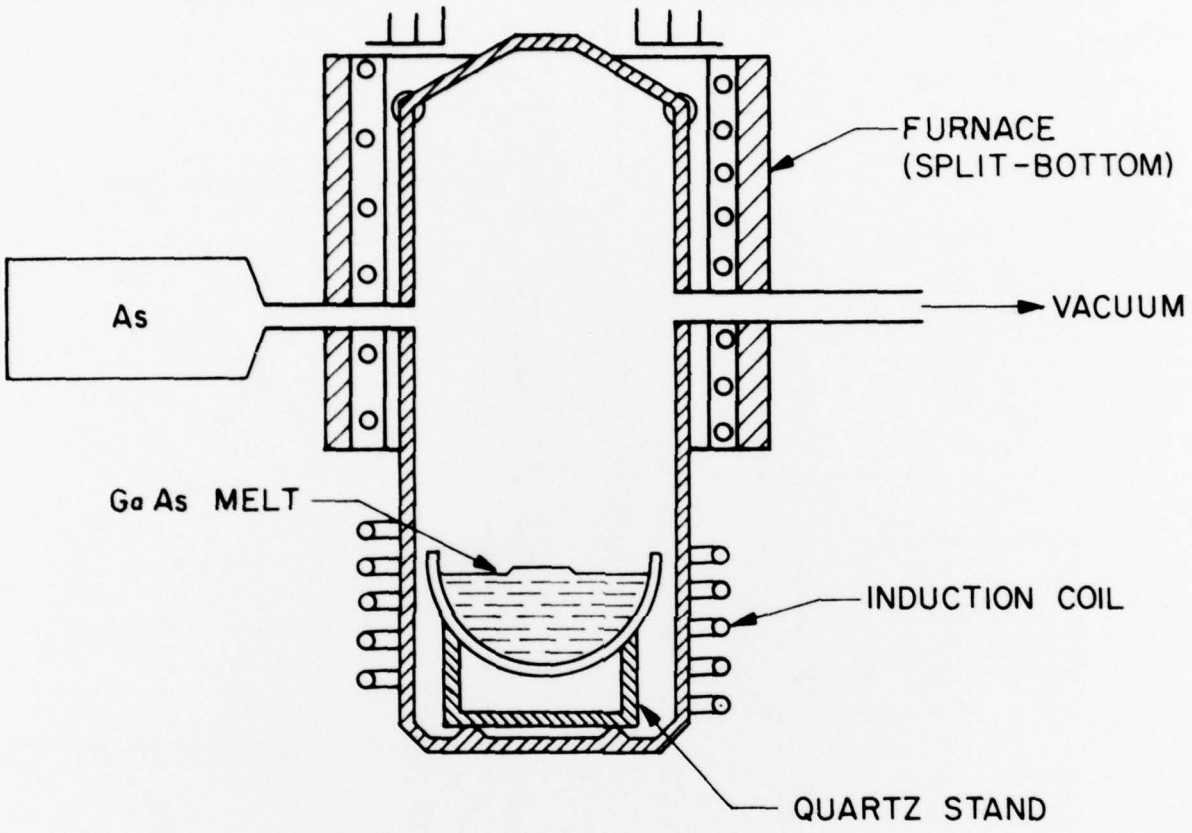


FIGURE 2. GaAs GROWER WITH NO PULLING APPARATUS

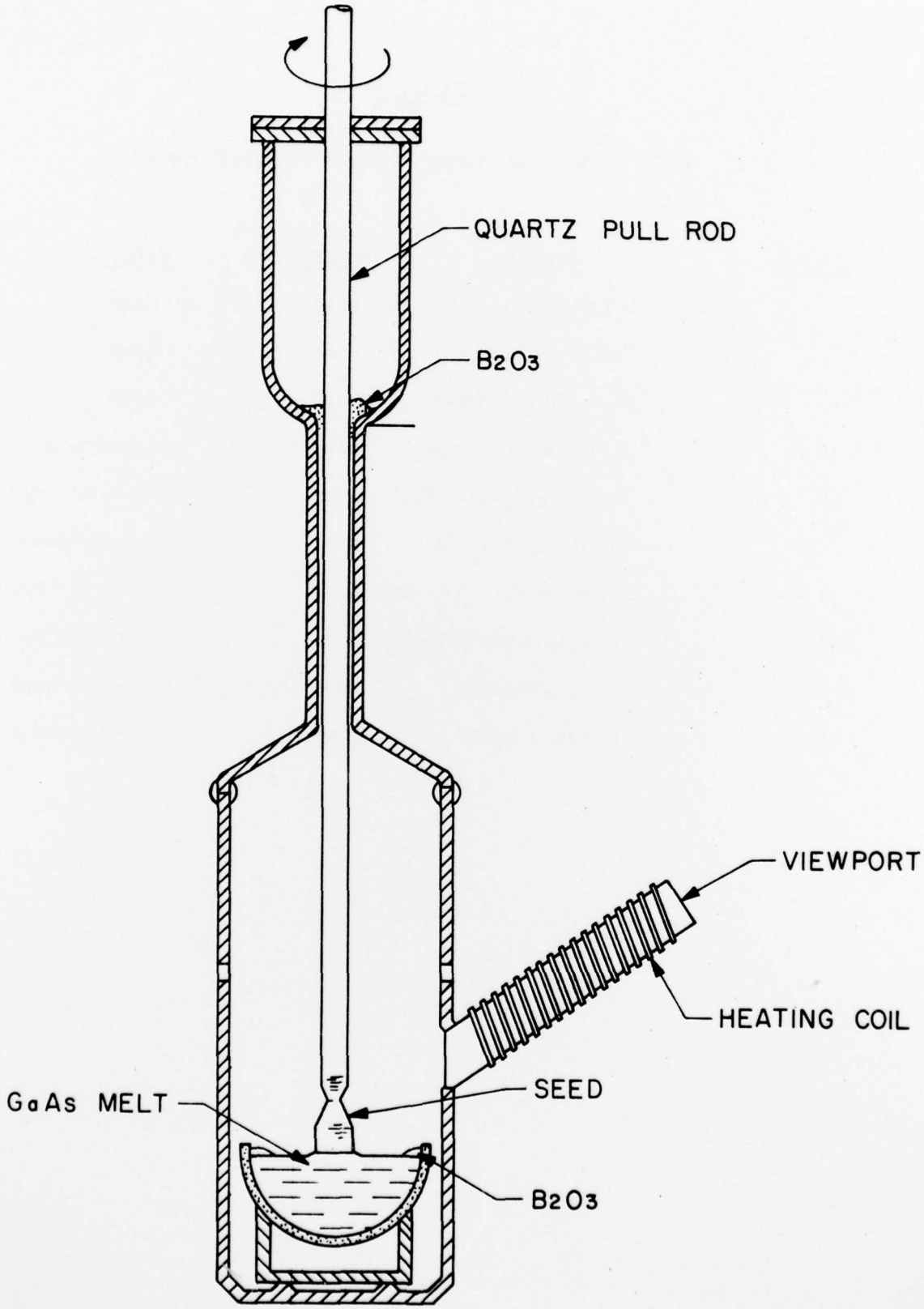


FIGURE 3. GaAs GROWER WITH VIEWPORT

TABLE 1

GaAs Growth Runs Using Various Crucible Materials

Run No.	Crucible	Dopants	Results
2	Boron Nitride (BN)	none	Good
5	Boron Nitride (BN)	none	Good
8	Boron Nitride (BN)	none	Good
12	Fused Quartz (SiO_2)	none	Si contamination
16	Aluminum Nitride (ALN)	none	Fractured Crucible
20	Fused Quartz (SiO_2)	none	Si contamination
21	Aluminum Oxide (AL_2O_3)	none	Fractured Crucible
22	Aluminum Oxide (AL_2O_3)	none	Fractured Crucible
24	Vitreous Carbon	none	Scum-like Deposit
25	Vitreous Carbon	none	Poor-thermal gradients

TABLE 2

Run No.	Dopant	Resistivity ohm-cm	Mobility $cm^2/v\text{-}sec$	Carrier Concentration n/cm^3	Comments
47	none	3.2×10^{-2}	3900	5.0×10^{16}	no B_2O_3
51	none	4.37×10^{-3}	3043	4.7×10^{15}	not pulled B_2O_3 used
52	none	10^7	-	-	not pulled B_2O_3 used
58	none	10^7	-	-	B_2O_3
60	none	10^7	-	-	B_2O_3
61	Cr	10^7	-	-	B_2O_3
63	Cr	10^7	-	-	B_2O_3
68	Zn	3.1×10^{-1}	2200	9×10^{16}	B_2O_3
69	Zn	1.0×10^{-1}	2130	1.6×10^{17}	no B_2O_3
72	Te	$5.1 \text{ z } 10^{-3}$	2900	4.3×10^{17}	no B_2O_3
77	Te	8.0×10^{-3}	2519	3.1×10^{17}	B_2O_3
78	none	1.3×10^{2}	5600	8.3×10^{12}	no gas torch - B_2O_3
79	Cr	10^7	-	-	viewport B_2O_3
80	none	10^7	5400	4.0×10^{10}	viewport B_2O_3

REFERENCES

1. R. Gremmelmaier, Z. Naturforsch. 11a (1956) 511.

2. J.L. Richards, J. Appl. Phys. 34 (1957) 289.

3. J.B. Mullin, B.W. Straughan and W.S. Brickwell, J. Phys. Chem. Solids 26 (1956) 782.

4. M.E. Weiner, D.T. Lassota and B. Schwartz, J. Electrochem. Soc. 118 (1971) 301.

5. J.B. Mullin, W.R. Macewan, C.H. Holliday and A.E.V. Webb, J. Cryst. Growth 13/14 (1972) 629.

MISSION
of
Rome Air Development Center

RADC plans and executes research, development, test and selected acquisition programs in support of Command, Control Communications and Intelligence (C^3I) activities. Technical and engineering support within areas of technical competence is provided to ESD Program Offices (POs) and other ESD elements. The principal technical mission areas are communications, electromagnetic guidance and control, surveillance of ground and aerospace objects, intelligence data collection and handling, information system technology, ionospheric propagation, solid state sciences, microwave physics and electronic reliability, maintainability and compatibility.

Printed by
United States Air Force
Hanscom AFB, Mass. 01731