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LIQUID ENCAPSULATED COMPOUNDING AND CZOCHRALSKI GROWTH OF SEMI---ETC(U)
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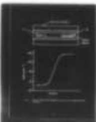
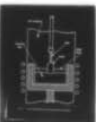

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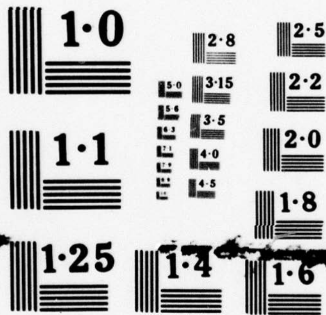

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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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LIQUID ENCAPSULATED COMPOUNDING AND CZOCHRALSKI GROWTH OF SEMI-INSULATING GALLIUM ARSENIDE FOR MICROWAVE/MILLIMETER-WAVE APPLICATIONS

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A wide variety of semiconductor devices utilizing gallium arsenide are currently under development by the military for use in secure communication, improved surveillance, and high speed digital logic systems. The GaAs field effect transistor, a critical component in these systems, is experiencing a rapidly expanding use in oscillator, mixer, logic element, power amplification, and low-noise/high-gain applications. However, the full potential of this device has not been realized, partly because of poor and unpredictable quality semi-insulating GaAs (cont'd)

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20. Abstract (cont'd)

substrates. More specifically, native defects, electrically active impurities, and diffusing charge traps are problems associated with commercial substrates. A silicon- and carbon-free modification of the liquid encapsulated Czochralski technique is described which yields high purity semi-insulating GaAs (approximately 10 to the 8th ohm-cm) without the intentional addition of charge compensators. The technique employs liquid encapsulated compounding of GaAs at nitrogen pressures to 100 atm, ultrapure elements, and pyrolytic boron nitride crucibles. A high pressure (135 atm) Varian HPCZ Czochralski crystal puller is employed for both compounding and crystal growth.

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LIQUID ENCAPSULATED COMPOUNDING AND CZOCHRALSKI GROWTH OF SEMI-INSULATING GALLIUM ARSENIDE FOR MICROWAVE/MILLIMETER-WAVE APPLICATIONS

INTRODUCTION

A wide variety of semiconductor devices utilizing gallium arsenide (GaAs) are currently under development by the military for use in advanced communication, surveillance, and target acquisition systems. GaAs, a compound semiconductor exhibiting a large energy bandgap, is characterized by a high intrinsic electron mobility (8600 $cm^2V^{-1}sec^{-1}$ @ 300 K) and resistivity (> 10^8 ohm-cm). The low-field electron mobility of GaAs is one of its greatest attributes and offers high frequency operation in devices such as the field effect transistor (FET). The technology of manufacturing high performance GaAs FET's is maturing at a rapid rate and the devices are experiencing a greatly expanding role in oscillator, mixer, logic element, power amplification, and low-noise/high-gain applications. However, the full potential and low-cost manufacture of GaAs FET's has yet to be realized, partly due to material problems experienced by substrate suppliers and device manufacturers.

It is commonly held by major GaAs FET manufacturers that the quality of semi-insulating substrates is one of the barriers to obtaining reliable, reproducible, and high performance devices. Recent studies[1-4] concerned with chromium-doped semi-insulating GaAs substrates point out that surface conversion during epitaxial processing, fast diffusing deep-level acceptors, carbon-arsenic vacancy complexes, and diffusing deep-level impurities are still observed. In order to minimize or eliminate the effect of these substrate imperfections on FET's fabricated by epitaxy, one must either grow a high quality buffer layer or reduce the impurity/defect levels contained in the starting materials and/or resulting from the growth process. The concentration of impurities and the stability of the substrates is even more critical to device performance when fabricating ion-implanted structures. Also, the formation of crystal dislocations and vacancies must be minimized during the growth of the GaAs boule. These material problems directly manifest themselves in the GaAs FET's electrical parameters and reliability, particularly its drift in gain characteristics. Not only do the devices exhibit both short- and long-term drift, but each device appears to have its own unique drift signature. A solution to the impurity and defect problems associated with Cr-doped semi-insulating GaAs grown by boat or liquid encapsulated Czochralski techniques is the objective of our program.

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1. E.M. Swiggard and H.H. Lessoff, "Electronic Material Technology (Semiconductors)," NRL Memorandum Report 3845, Naval Research Laboratory, August 1978.

2. J.M. Ballantyne, Army Research Office Scientific Services Program, Report No. 0487, January 1978.

3. B.D. McCombe, "Characterization of III-V Materials," NRL Memorandum Report 3701, Naval Research Laboratory, February 1978.

4. B. Tuck, G.A. Adegoboyega, P.R. Jay, and M.J. Cardwell, "Out-Diffusion of Chromium from GaAs Substrates," Proceedings of 7th International Symposium on GaAs, St. Louis, Mo., September 1978.

CRYSTAL GROWTH

Gallium arsenide, a III-V compound semiconductor, has the zinc blende-structure consisting of two interpenetrating face centered cubic (fcc) sublattices. One fcc sublattice describes the position of the Ga atoms and the other, As atoms. The technology involved in the growth of GaAs is considerably more complicated than that employed for silicon, for one is dealing with more complicated binary phase equilibria and a highly volatile component, arsenic. Exact stoichiometry of the GaAs compound must be maintained during the growth process in order to achieve high mobility and crystal perfection, requiring precise control of the As vapor pressure in the chosen growth system.

The bulk compound is normally formed by the reaction of As vapor with Ga metal at elevated temperatures in sealed quartz ampoules as shown in Fig. 1. Typically, an As reservoir contained at one end of the ampoule is heated to 600 C. This generates approximately 1 atm of As vapor pressure in the system, a prerequisite for obtaining stoichiometric GaAs.[5] The As vapor reacts with Ga metal maintained at $\sim$ 1260 C and located at the other end of the ampoule in a quartz boat. After the Ga has been completely reacted, single crystal growth may be initiated by programmed cooling (gradient freeze) or by physically moving either the ampoule or furnace to provide proper temperature gradients for growth (horizontal Bridgman). This indirect approach (As transport) for the compounding and growth of GaAs is used because of the high vapor pressure of As at its melting point and at the melting point of GaAs, $\sim$ 20 atm at 812 C, and $\sim$ 60 atm at 1238 C, respectively.

Another approach to the commercial production of bulk GaAs which is gaining favor is the liquid encapsulated Czochralski technique (LEC CZ). Metz et al[6] first described the use of an encapsulant to suppress the loss of a volatile component from a melt. In their method, Pb, Te, and B_2O_3 were placed in a crucible and heated to form PbTe covered by a thin layer of molten B_2O_3. A pressure of 1 atm was then used to reduce vaporization of the melt during the growth of PbTe single crystals. Mullin et al[7] reported on the use of this method (called Liquid Encapsulated Technique) for the growth of InAs and GaAs from stoichiometric melts. In this method, shown in Fig. 2, the vaporization of As from molten GaAs is inhibited by placing a layer of a nonreactive encapsulant on the melt surface. An inert gas pressure which is higher than the As vapor pressure is then maintained over the molten B_2O_3 layer. A rotating seed crystal contacting the molten GaAs is then slowly withdrawn through the liquid encapsulant while the temperature is regulated to obtain the desired diameter crystal. A drawback to the conventional LEC CZ technique is the fact that the GaAs polycrystalline source

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5. L.R. Weisburg, F.D. Rosi, and P.G. Herkart, "Properties of Elemental and Compound Semiconductors," (Interscience Publishers, New York, 1959) p. 31.

6. E.P.A. Metz, R.C. Miller, and R. Mazelsky, "A Technique for Pulling Single Crystals of Volatile Materials," J. Appl. Phys. 33, 2016 (1962).

7. J.B. Mullin, B.W. Straughan, and W.S. Brickell, "Liquid Encapsulation Techniques: The Use of an Inert Liquid in Suppressing Dissociation During the Melt-Growth of InAs and GaAs Crystals," J. Phys. Chem. Solids 26, 782 (1965).

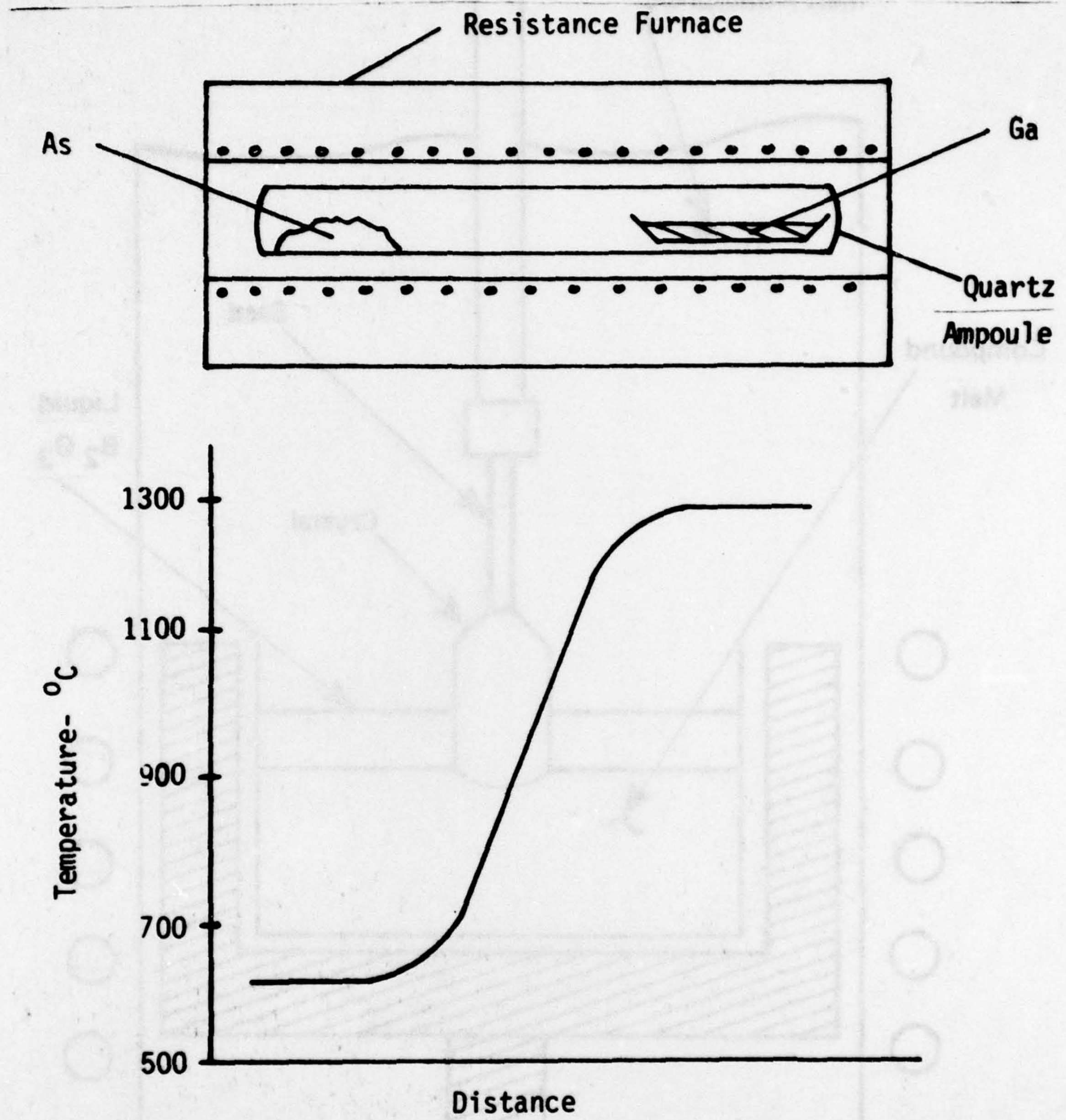

Fig. 1. Typical furnace and temperature profile for compounding GaAs in quartz.

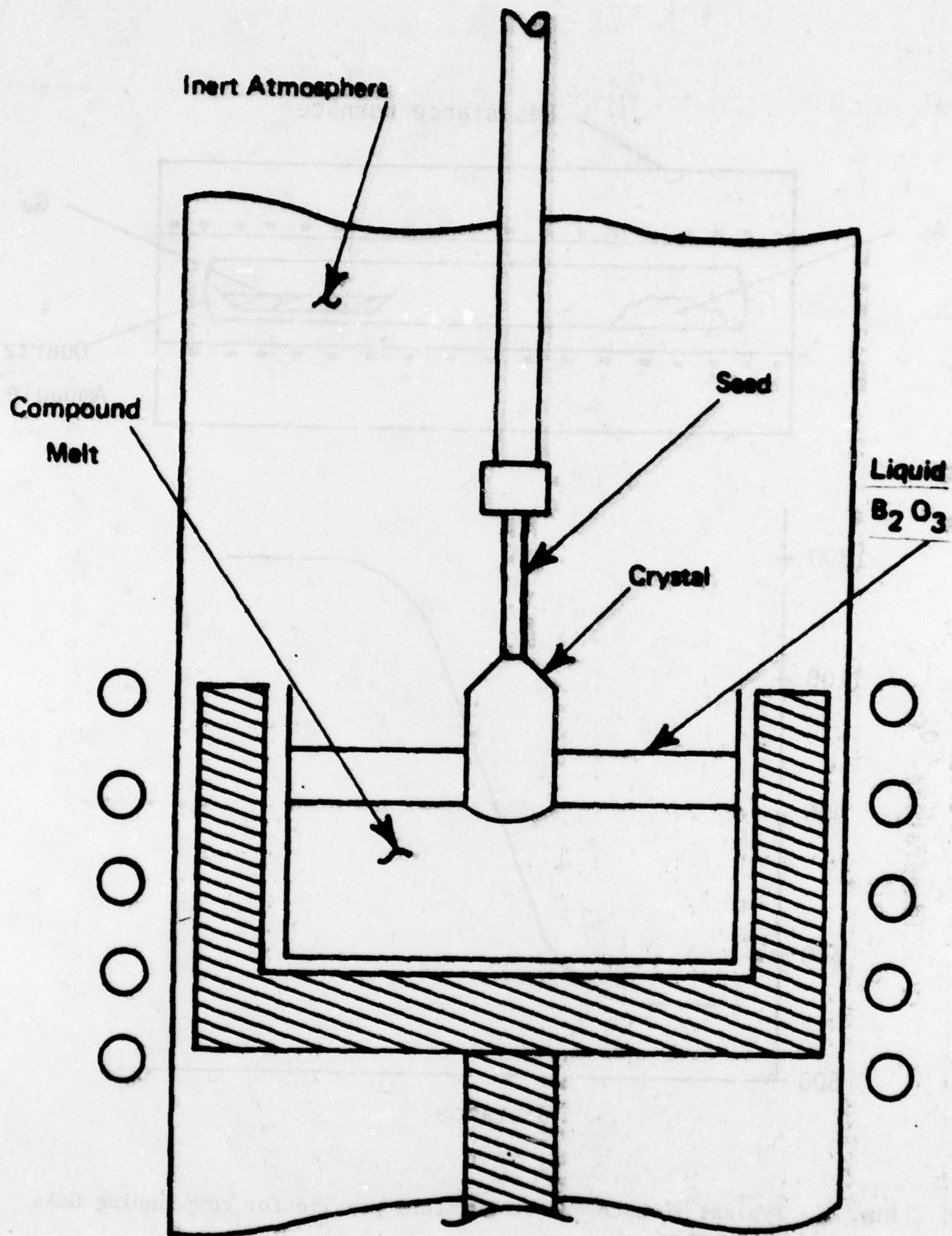

Fig. 2. Liquid encapsulated Czochralski pulling technique.

material from which the crystal is pulled, is normally compounded in quartz ampoules. Also, the etch pit density (EPD) of GaAs grown by the LEC CZ technique is generally higher than that of gradient freeze grown material, typically 10^4-10^5, and 1-$5x10^3/cm^2$, respectively. However, it has been shown by Antypas[8] that by careful control of LEC CZ growth conditions, one may achieve EPD's considerably lower than boat grown material (< $100/cm^2$).

The use of quartz as a container for Ga, As, and molten GaAs, and as a reaction vessel can lead to appreciable silicon contamination.[9] Since silicon can act as a shallow donor or acceptor in GaAs,[10] incorporation can preclude one from attaining high purity, uncompensated semi-insulating substrates. Various schemes have been used to reduce the dissociation of the quartz components or screen the melt from the reaction products and volatile oxides in order to suppress silicon contamination. These include deliberate introduction of oxygen[11] and addition of gallium oxide.[12] The use of a pyrolytic boron nitride (PBN) boat and liner in the quartz ampoule was reported by Swiggard et al[13] to reduce the level of silicon impurities introduced into GaAs during compounding. However, most schemes in use still add impurities from the devitrification and/or chemical attack of the quartz ampoule. Chromium, a deep-level acceptor and/or oxygen, a deep-level donor, are normally used to compensate the various shallow donors/acceptors in GaAs, thereby making it semi-insulating (> 10^8 ohm-cm).

The conventional liquid encapsulated Czochralski technique for growing single-crystal GaAs is a process consisting of two separate steps - compounding and subsequent crystal growth. However, because of increased handling, the technique can introduce more impurities than boat methods. The development of a process which incorporates both steps and which is capable of growing high purity, thermally stable, semi-insulating GaAs substrates would be of considerable importance to microwave, millimter-wave IC, and high speed logic device manufacturers.

Pekarek[14] described a process for synthesizing GaAs in a Czochralski puller at nitrogen pressures to 1.5 atm. Arsenic contained in a quartz ampoule was vaporized and transferred via a quartz tube into heated Ga covered by molten B_2O_3. High mobility, low carrier concentration single

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8. G.A. Antypas, "LEC Czochralski Growth of GaAs and InP for Microwave Applications," Fourth Biennial Conference: Active Semiconductor Devices for Microwaves and Integrated Optics, Cornell University, Ithaca, New York (1975).

9. J.W. Harrison, "A Survey of Single Crystal Growth Methods for Gallium Arsenide," Solid State Technology 16, No. 1, 48 (1973).

10. S.M. Sze, and J.C. Irvin, "Resistivity, Mobility, and Impurity Levels in GaAs, Ge, and Si at 300°K," Solid State Electronics 11, 599 (1968).

11. N.G. Ainslie, US Patent #3,353,912.

12. J.M. Woodall, US Patent #3,322,501.

13. E.M. Swiggard, S.H. Lee, and F.W. Von Batchelder, Proceedings of the Sixth Gallium Arsenide and Related Compounds Conference (St. Louis), Institute of Physics, Bristol, England, 1977, p. 23.

14. L. Pekarek, "Apparatus for Synthesis of Gallium Arsenide Under Liquid Encapsulant," Czech. J. Phys. 20, 857 (1970).

crystals of GaAs were prepared by this method. Haggerty and Wenckus[15] reported the successful synthesis of GaAs from the elements under molten B_2O_3 at pressures to 54 atm, but did not pull directly after compounding. The in-situ LEC compounding/Czochralski growth process we describe for growing semi-insulating GaAs eliminates all dependence on quartz and carbon components, and reduces or eliminates the requirement for chromium compensation. This is accomplished by reacting elemental gallium and arsenic under a molten encapsulant in PBN crucibles at nitrogen pressures to 100 atm. A specially designed high-pressure Czochralski crystal pulling system, Varian model HPCZ, was used for maintaining the nitrogen gas ambient and for growth of the bulk GaAs crystals (see Fig. 3). This system contains provision for the following: rotation of the crystal and/or crucible; raising and lowering of the crystal and/or crucible; remote control of temperature, gas flow, pulling and rotation rates; TV process monitoring; cryo fore-pumping; vac-ion pumping to 10^{-5} torr; hydraulic lifting of the chamber; and is designed for operation at pressures to 135 atm with neutral, oxidizing or reducing ambients. Facilities installed to support this system include high-purity water and nitrogen gas, vacuum drying, and a dust-free fume hood with rinse tanks.

The in-situ LEC compounding and Czochralski growth of GaAs was carried out in the following manner. Stoichiometric quantities of high-purity gallium and arsenic totaling up to 300 grams were weighed and placed in PBN crucibles approximately 5 cm in diameter. The crucibles were cleaned prior to loading by etching in a 1:1 solution of electronic grade HCl and de-ionized water for 10 minutes. After etching, the crucibles were rinsed with de-ionized water, methanol, and vacuum dried overnight at 200 C. The loaded crucibles were placed in carbon coated graphite or tantalum susceptors in the Czochralski pulling chamber. A 450-kHz radio frequency induction unit was used for heating. A dehydrated pellet of boron oxide encapsulant, weighing approximately 30 grams, was placed on top of the charge as shown in Fig. 4. When molten, this pellet provided an encapsulant depth of approximately 1.0 cm.

The moisture content of the boron oxide encapsulant was found to be related to the growth of high-quality, twin-free single crystals of GaAs. If the boron oxide contained an excessive amount of moisture, bubbles were continuously formed by the reaction of this moisture with the GaAs melt. These bubbles formed at the melt/encapsulant interface and subsequently rose to the surface releasing arsenic. This led to nonstoichiometric arsenic-deficient GaAs melts which promoted twinning of the crystals. Although the "as-received" pellets of boron oxide appeared to be completely dehydrated, they still contained a considerable amount of moisture, and use was generally unsatisfactory. An oil-free, high-vacuum baking system was constructed to further dehydrate the pellets. Heating the boron oxide to $\sim$ 1,000 C at 10^{-7} torr in induction heated platinum/gold crucibles was found to give satisfactory results. After cooling to room temperature, the pellets were easily removed and placed on top of the charge in the pulling chamber.

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15. J.S. Haggerty and J.F. Wenckus, "Development of Techniques for the Growth of Bulk Single Crystals of Several III-V Compound Semiconductors," Final Technical Report, Contract No. NAS 12-2020 (1970).

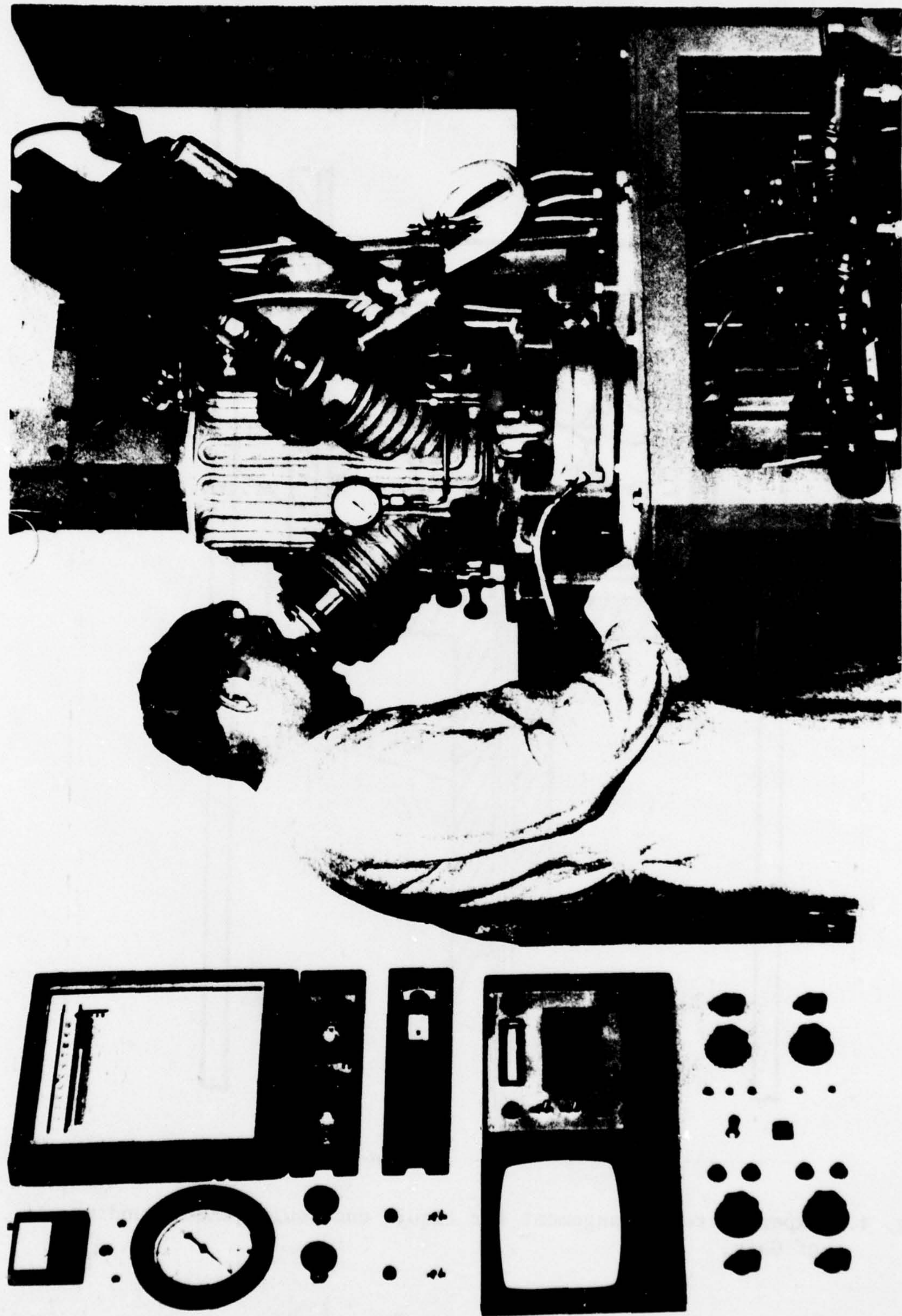

Fig. 3. High pressure Czochralski crystal pulling system (Varian model HPCZ).

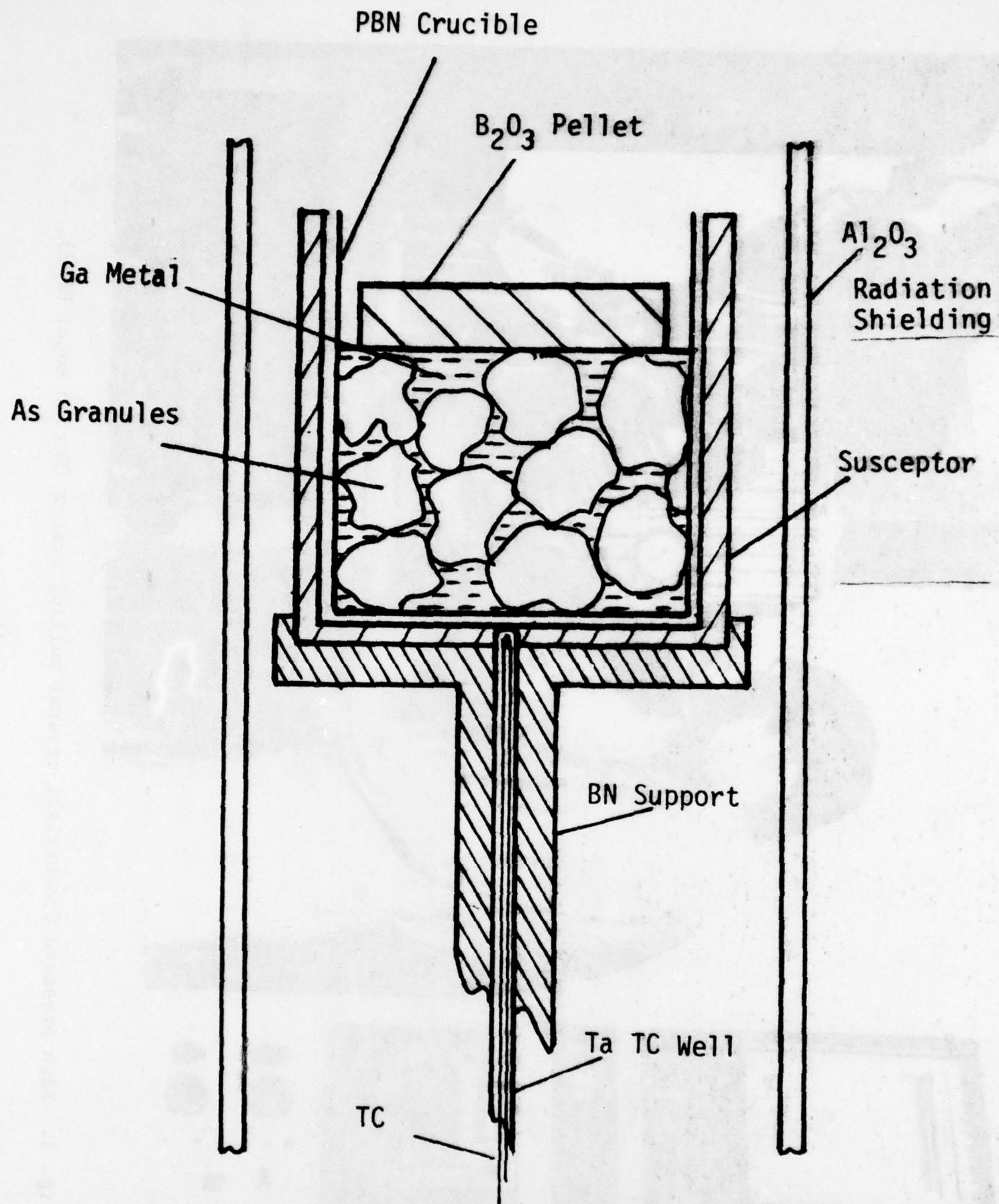

Fig. 4. Experimental arrangement for liquid encapsulated compounding of GaAs.

After the growth station was established (susceptor, crucible, gallium, arsenic, boron oxide, etc.) and the chamber closed, the system was evacuated to 10^{-5} torr. The charge was then slowly heated to 325 C to remove residual moisture and volatile gallium/arsenic oxides. If the temperature exceeded 325 C, significant amounts of arsenic were lost by volatilization prior to compounding. After several hours, the system was then backfilled with high-purity nitrogen gas to 3.4 atm and the temperature increased to 450 C. During this step, the boron oxide melted and flowed into the voids. The nitrogen gas was obtained by vaporizing liquid nitrogen and then charging storage tanks to 100 atm with an oil-free, high pressure booster pump. After the boron oxide was completely melted, the pressure in the pulling chamber was increased to the level used during compounding. The pressure of the nitrogen gas was found to influence the yield of GaAs, e.g., at 40 atm a yield of $\sim$ 90% was obtained with the remainder of the arsenic lost from the crucible. At nitrogen overpressures of 60 atm and above, yields of 99^+% were obtained. The reaction was indicated by a rapid temperature rise when the crucible approached 700 C and could be observed on the TV monitor.

Single crystals of GaAs were grown from the in-situ compounded material by the LEC CZ technique as previously shown in Fig. 2. All crystals were grown in the <111> B direction (arsenic face towards the melt) on seed material supplied by Laser Diodes, Inc. Nitrogen gas pressures of 1.0 to 20.0 atm and pulling rates of 1.0 to 2.0 cm/hr were used during growth. Both concurrent and countercurrent rotation of crucible and crystal were used at rates of 5 and 15 rpm respectively. The rotation direction of the crystal and crucible had a bearing on the shape of the melt/crystal interface in our system, concurrent rotation producing a more convex interface. A single crystal grown from LEC compounded GaAs is shown in Fig. 5.

ELECTRICAL MEASUREMENTS

The measurements of resistivity, mobility and Hall coefficient were performed by using the van der Pauw method[16] with an automated dc system (Fig. 6). The van der Pauw technique is unique in that it requires only four contacts located anywhere on the periphery of a uniformly thick sample of arbitrary shape. However, the gain realized by reduced sample contacting and geometrical constraints is offset by the necessity that current and voltage leads be interchanged between different pairs of contacts. Various sample configurations have been devised to minimize the requirement that the electrical contacts be of a finite size and located at the sample's circumference.[17] In this work, the conventional "clover-shaped" sample geometry was replaced by a "Greek-cross" structure which has been shown to be a valid van der Pauw configuration provided the arm length is equal to or greater than the arm width.[18]

The resistivity, ρ, in ohm-cm is given by

$$\rho = \frac{\pi t}{\ln 2}\left(\frac{R_{AB,CD} + R_{BC,DA}}{2}\right) F \qquad (1)$$

---

16. L.J. van der Pauw, Philips Rsch Reports 13, 1-9 (1958).

17. L.J. van der Pauw, Philips Tech. Rev. 20, 220-224 (1958/1959).

18. J.M. David and M.G. Buehler, Solid-State Electron., to be published.

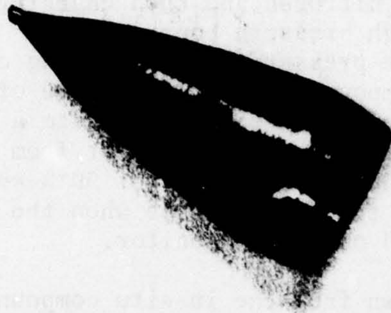

Fig. 5. Single crystal and compounded charge of semi-insulating GaAs.

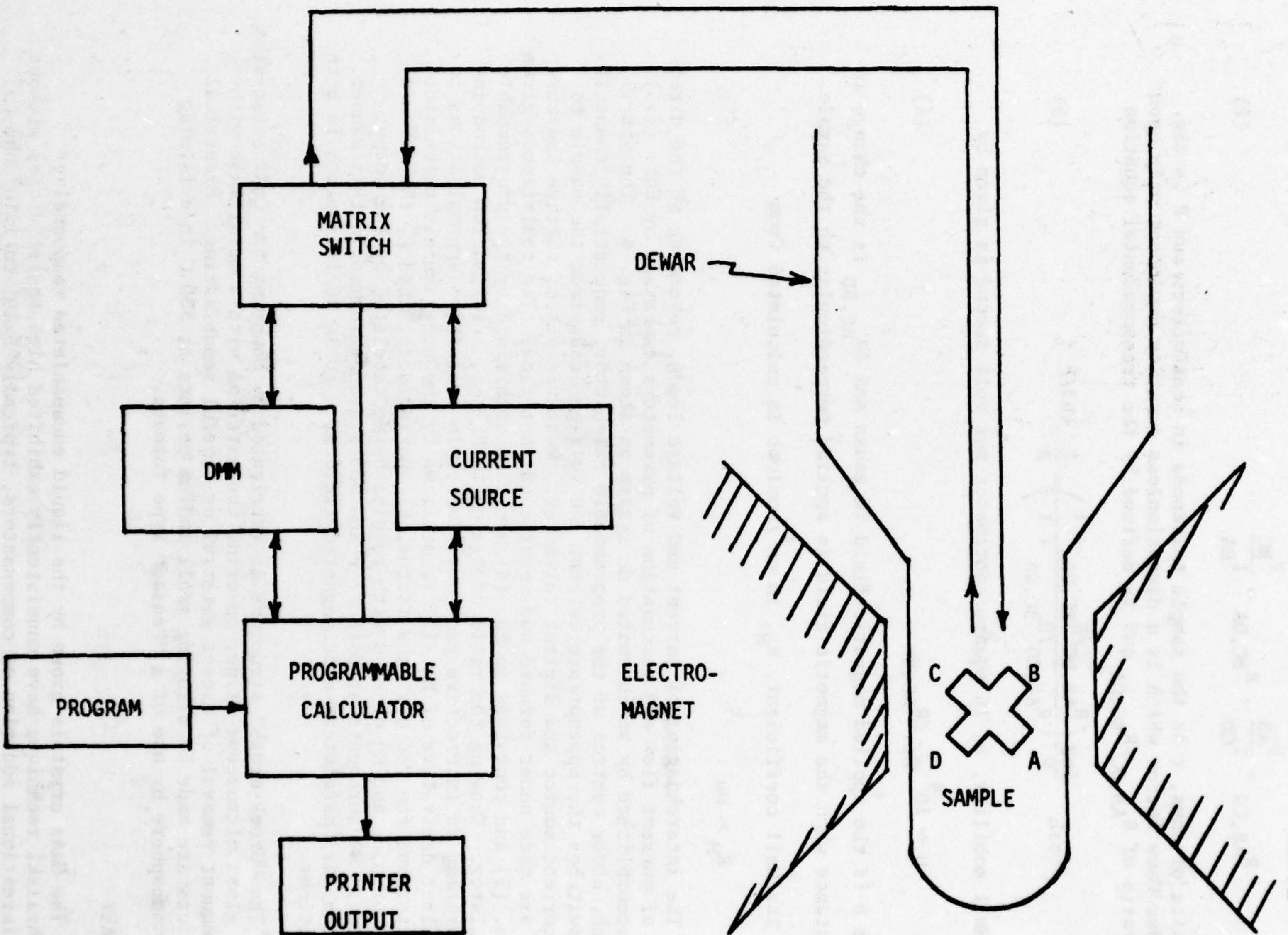

Fig. 6. Automated van der Pauw Hall and resistivity system.

where

$$R_{AB,CD} = \frac{V_{AB}}{I_{CD}} , R_{BC,DA} = \frac{V_{BC}}{I_{DA}} \quad (2)$$

in units of ohms, t is the sample thickness in centimeters, and F is the van der Pauw factor which is a dimensionless quantity dependent only upon the ratio of $R_{AB,DC}/R_{BC,DA}$ and is defined by the transcendental equation

$$\cosh \frac{\ln 2}{F}\left(\frac{R_{AB,DC}/R_{BC,DA} - 1}{R_{AB,CD}/R_{BC,DA} + 1}\right) = \frac{1}{2} e^{\ln 2/F} . \quad (3)$$

The Hall mobility, μ, in square centimeter per volt second is given by

$$\mu = 10^8 \frac{t}{B\rho} \Delta R_{AC,BD} \quad (4)$$

where B is the applied magnetic field in gauss and $\Delta R_{AC,BD}$ is the change in resistance when the magnetic field is applied perpendicular to the sample.

The Hall coefficient, R_H, in cm^3/coulomb is calculated from

$$R_H = \rho\mu . \quad (5)$$

The interchanging of current and voltage leads, reversing of the direction of current flow and calculation of parameters expressed by Eqs. (1-5) are accomplished by an automated dc system as shown in Fig. 6. The matrix switch, under control of the programmable calculator, sequentially connects and switches the appropriate current and voltage leads from the sample to the current source and digital voltmeter. Measurements of voltage and current are made under forward and reverse current flow. The resistances given by Eq. (2) and contained in Eq. (4) are then determined by the programmable calculator. Knowing the ratio of $R_{AB,CD}$ to $R_{BC,DA}$, a relaxation method incorporating an interactive procedure to obtain successive approximations to the first derivative of Eq. (3) is utilized by the programmable calculator to determine the van der Pauw factor, F. Having determined F, the calculations of ρ, μ and R_H proceed with results being tabulated by the output printer. Measurements at both 77 K and 300 K are performed in this manner. For the Hall parameters a dc magnetic field of 5 to 10 kG is applied in both directions.

The "Greek-cross" structure is fabricated by mounting the GaAs substrates on a glass microscope slide, covering the material with a metal mask with subsequent removal of excess material by careful sandblasting. Electrical contacts are made by alloying small indium pellets at 350 C in a forming gas atmosphere by use of a "Penzac" type furnace.

SUMMARY

The GaAs crystals grown by the liquid encapsulated compounding/Czochralski technique have consistently exhibited high resistivities without the intentional addition of compensators, typically $5x10^7$ to $1x10^8$ ohm-cm. Substrates fabricated from these crystals are presently being evaluated by utilizing epitaxial and ion-implantation qualification procedures. The

one-step or "in-situ" compounding/growth of GaAs which we have described in this report is believed to be the best approach to solving the current problems associated with semi-insulating substrates. Various semiconductor device and equipment manufacturers such as Varian Associates, Westinghouse, Hughes, Rockwell, Microwave Associates, and Metals Research are in the process of, or have purchased/constructed the equipment to grow semi-insulating GaAs by this technique.[19]

19. Private communications.