

AD-A115 810

CRYSTAL SPECIALTIES INC MONROVIA CA

F/G 20/2

HIGH-PRESSURE GRADIENT-FREEZE GROWTH OF SINGLE CRYSTALS OF INDI--ETC(U)

APR 82 W P ALLRED

F19628-81-C-0038

NL

UNCLASSIFIED

RADC-TR-82-64

for 1

DATA
1980



END

DATE

FILED

07-82

DTIC

AD A115810

RADC-TR-82-84
Final Technical Report
April 1982



12

HIGH-PRESSURE GRADIENT-FREEZE GROWTH OF SINGLE CRYSTALS OF INDIUM PHOSPHIDE

Crystal Specialties, Inc.

Worth P. Allred

DTIC
ELECTE
JUN 21 1982
S B

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

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

DTIC FILE COPY

82 06 21 106

This report has been reviewed by the RADC Public Affairs Office (PA) 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-82-64 has been reviewed and is approved for publication.

APPROVED:

Joseph A. Adamski

JOSEPH A. ADAMSKI
Project Engineer

APPROVED:

Harold Roth

HAROLD ROTH
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 01731. This will assist us in maintaining a current mailing list.

Do not return copies of this report unless contractual obligations or notices on a specific document requires that it be returned.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-82-64	2. GOVT ACCESSION NO. AD-A115 810	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) HIGH-PRESSURE GRADIENT-FREEZE GROWTH OF SINGLE CRYSTALS OF INDIUM PHOSPHIDE		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 1 Jan 81 - 15 Aug 81
		6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) Worth P. Allred		8. CONTRACT OR GRANT NUMBER(s) F19628-81-C-0038
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 62702F 46001732
11. CONTROLLING OFFICE NAME AND ADDRESS Deputy for Electronic Technology (RADC/ESM) Hanscom AFB MA 01731		12. REPORT DATE April 1982
		13. NUMBER OF PAGES 9
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 10 to the 16th power cc		
18. SUPPLEMENTARY NOTES RADC Project Engineer: Joseph A. Adamski (ESM)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) High Pressure Synthesis Stoichiometric Indium Phosphide Indium Phosphide III-V Semiconductor Compound Phosphorous		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Large polycrystalline InP ingots weighing up to 2,000 gms have been compounded in a gradient-freeze internally pressure balanced growth system. Ingots grown in the system have an impurity level of about 2×10^{-16} atoms/cm ³ . This system promises to be a method by which polycrystalline and possibly single crystals can be grown in a few hours and at a reasonable cost.		

DD FORM 1473

JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SUMMARY

The principal objective of this work was to produce large single crystals of indium phosphide in a high-pressure, gradient-freeze, internally pressure balanced growth system.

The growth system was developed on a prior contract. It consists of a horizontal gradient-freeze furnace mounted inside a steel pressure vessel, and incorporates an automatic pressure balancing system which maintains a pressure of nitrogen inside the steel vessel equal to the pressure of phosphorus inside the growth ampoule. In this way, the hazard of ampoule explosions caused by the high phosphorus vapor pressure is reduced. The growth system and associated pressure balancing system were described in the Final Report on Contract No. F19628-79-C-0096. (1)

It was a second objective of this work to produce doped single crystals of InP and determine the segregation coefficients of the more common dopants.

The principal problem was the presence of an oxide layer floating on the surface of the melt. The oxide caused the spurious nucleation of many crystal grains, preventing the growth of single crystals.

The effort in this work was directed toward methods of removing the oxide. It was found that essentially all of the oxide on molten indium could be removed by heat-treatment in flowing hydrogen at 1100° C for 16 hours. However, when the hydrogen-purified indium was reacted with phosphorus in the growth system prior to crystal growth, an oxide layer was observed floating on the InP. This oxide presumably was the result of oxygen contamination of the phosphorus, and the program was terminated before this problem could be resolved.



1/ii

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

PREFACE

This report describes research and development efforts on an internally pressure-balanced method of growing crystals of indium phosphide. The program was the third phase of an effort sponsored by the Deputy for Electronic Technology (RADC), Hanscom Air Force Base, MA.

Most of the effort on the first phase was devoted to the design and construction of the growth and pressure balancing systems and to preliminary InP synthesis and growth runs to evaluate the apparatus and the method. That work was reported in the Final Technical Report on Contract No. F19628-77-C-0105 (2). Modifications to the apparatus, based on the findings of the first phase of the work, were described in Reference 1. Large, dense polycrystalline ingots of stoichiometric InP can now be produced. However, the growth of single crystals has been severely hindered by the presence of oxides floating on the melt.

Worth P. Allred was the Principal Investigator on the program for Crystal Specialties, Inc. Contributing to various aspects of the work were James W. Burns, Martin Kapelowitz, and William L. Hunter. Joseph A. Adamski was the Project Scientist for Rome Air Development Center.

TABLE OF CONTENTS

	Page
1. Introduction	1
2. Crystal Growth	1
3. Hydrogen Heat-Treatment of Indium	4
4. Conclusions	5
5. Recommendations	5

1. INTRODUCTION

Several methods of growing single crystals of indium phosphide were evolved earlier by other workers. These methods include growth from dilute solution (3); growth through vapor phase chemical reactions (4); high-pressure horizontal gradient-freeze systems (5, 6); and high-pressure liquid encapsulated (LEC) Czochralski pulling (7). Of these, only the last two methods have yielded relatively large single crystals in reasonably short growth times, and it should be noted that both methods involve the use of high pressures.

The approach adopted in the present work has been described previously (1). Polycrystalline ingots of InP weighing several hundred grams have been produced, but none of the growth runs yielded completely single crystals.

The principal problem impeding single crystal growth was the presence of an oxide layer floating on the surface of the melt. Convection currents in the melt caused the oxide layer to move to the cooler end of the boat where it contacted the seed. This made it impossible to maintain single crystal growth off the seed.

Since an oxide film was always observed on the as-received indium when it was melted, experiments were conducted to devise means to remove the oxide from the indium. These experiments were successful, and are described in Section 3 of this report. However, an oxide film was still observed on molten InP after reacting the purified indium with phosphorus. Presumably, this was the result of oxygen contamination of the phosphorus. The program was terminated before means were devised to eliminate this cause of floating oxides.

2. CRYSTAL GROWTH

The ampoule loading and crystal growth techniques were similar to those reported on previously (1). In the first growth run of the present work, (Run No. 142) 56.6 gms of six-nines pure red phosphorus were placed at the bellows end of the ampoule. An additional 77.0 gms of phosphorus were

loaded into the ampoule to provide the phosphorus overpressure. The mass of indium loaded into the quartz growth boat was 209.8 gms. No seed was used in this run.

The growth ampoule was evacuated to 5×10^{-6} Torr with the Cryopump, and the indium was vacuum heat-treated at 800°C for three hours. After seal-off, the ampoule was loaded into the gradient freeze furnace and the pressure vessel was closed. The indium and phosphorus were reacted to form an InP melt in $2\frac{1}{2}$ hours, and the melt was then allowed to soak and homogenize for four hours. Since no seed was used in this run, the melt temperature at the cooler end of the boat was gradually reduced manually until freezing of the InP at the cooler end occurred. The temperature was then increased slowly to melt back, the objective being to melt all of the crystallites except the one at the coolest part of the boat. This technique can sometimes be used to advantage to obtain a small seed on which to grow a single crystal. It was not successful in this instance however, but it appeared that not more than two or three dendrites were present when programmed cooling was initiated.

The Data-Trak was programmed to cool the melt at a rate of 1.5°C/hr , and the programmed cooling continued for 29 hours, after which the furnace power was shut off. The temperature gradient used was approximately 10°C/in. , and the phosphorus pressure at the beginning of the programmed cooling was 390 psig. A dense polycrystalline ingot of InP weighing 263 gms was obtained.

Run No. 143 was very similar to No. 142, and again no seed was used. The technique of melting back after freezing the top surface at the front end was used in an attempt to isolate one grain on which to grow a crystal, but again the result was a polycrystalline ingot. The cooling rate used was 1.5°C/hr , and the ingot obtained weighed 229 gms.

Indium phosphide seeds, cut from the polycrystalline boules already obtained, were used in the next two runs, Nos. 144 and 145. These seeds were oriented in the $[111]$ direction. Additionally, the indium used in these two

runs was heat treated in hydrogen for three hours at 800°C prior to loading.

Run No. 144 was cooled at a rate of 2°C/hr for 24 hours. The growth rate off the seed was quite rapid, and it was not possible to maintain single crystal growth; the crystal "broke down" to polycrystalline growth at the shoulders of the boat. This was most likely due to the oxides which could be observed floating on the melt, rather than too rapid a growth rate.

In run No. 145 we inadvertently melted the seed. This run, like No. 144, was programmed to cool at a rate of 2°C/hr . Oxides again were present, and as mentioned earlier, the ingot was polycrystalline.

In the next attempt, run No. 146, polycrystalline InP from previous runs was used as the starting material, together with 85 gms of excess phosphorus added to the ampoule to provide the phosphorus overpressure. Using pre-reacted InP rather than the elements themselves gave a cleaner melt surface, but there was still some oxide floating on the melt, and the result was a polycrystalline ingot. The cooling rate in this run was one degree per hour, and the Data-Trak program unit cooled the system at that rate for 40 hours.

The last two runs made during the work used indium which had been purified in flowing hydrogen for 16 hours as described in the next section of this report. This indium was free of any oxide; the hydrogen heat-treatment to reduce the indium oxide was accomplished after the indium and phosphorus had been loaded into the growth ampoule. However, after reacting with the phosphorus to form InP, an oxide film again was observed on the melt surface. This was presumably the result of oxygen contamination of the phosphorus.

These last two runs, using purified indium, were unseeded. As discussed in the following section, the hydrogen heat treatment of the indium was done at 1100°C , and since this was carried out after loading the growth ampoule, a seed would have decomposed had one been used. In view of the oxide layer in these last runs, it is highly unlikely that single crystal growth could have been achieved even had a seed been used.

3. HYDROGEN HEAT-TREATMENT OF INDIUM

Experiments were performed to determine the time and temperature required to remove the oxide from 400 gm charges of molten indium with flowing hydrogen.

A vacuum-gas manifold incorporating air operated valves and a palladium purifier for the hydrogen was used in this work. An ampoule containing indium in a quartz boat was first evacuated with the Cryopump. It was then filled with ultra-pure nitrogen. When the pressure of nitrogen inside the ampoule reached one atmosphere, an air-operated vent valve in the manifold was opened, and the ampoule was flushed with nitrogen for five minutes. An automatic programmer then closed the nitrogen valve and opened the hydrogen valve. The hydrogen was burned as it exhausted from the vent.

The temperature of the indium was raised to 1100°C , and the system was held at that temperature, with the hydrogen flowing, for six hours. After cool down, the ampoule was flushed with nitrogen, and the boat and the indium were removed for examination. There was still some oxide film, easily discernible to the eye, on both ends of the upper surface of the indium bar, extending about one-fourth of the way toward the center of the bar. The center portion of the bar was clean. During hydrogen heat treatment, the oxide divides at the center of the bar, and the films migrate toward the ends, where the temperature is lower. The indium was welded to the boat, having wetted the quartz.

The boat was placed back in the ampoule, and the procedure was repeated, but this time the indium was held at 1100°C for ten hours. At the end of this time the only trace of contamination left on the indium was a very small quantity of white ash at one end of the boat. This material was not attached to the indium, but fell out of the boat when the latter was turned over. Furthermore, the indium also dropped free of the boat. This was highly encouraging, since the indium was stuck to the boat after the first six hours. The fact that the indium dropped out of the boat after 16 hours was a n

indication that the oxides were completely reduced by the hydrogen heat treatment.

After exposure to the room air for fifteen minutes, the indium was again sealed in the ampoule and melted. As expected, an oxide film was present. The indium cannot be heat-treated in flowing hydrogen at 1100°C with an InP seed in the boat, since the seed would decompose. It is apparent, therefore, that the indium would have to be kept under nitrogen after heat-treating and during loading of the InP growth ampoule.

We also attempted to remove the oxide film by simple vacuum baking, but this failed. The temperature was not raised above 1020°C in this experiment because too much indium was being lost from the boat by evaporation. After three hours the furnace power was shut off. The indium which evaporated from the boat collected in droplets on the wall of the ampoule and ran to the bottom, where it collected at the ends of the boat. On cool down, this indium welded the boat to the ampoule, and it was impossible to separate the two without prolonged soaking in HCl. In addition, the indium in the boat was stuck to the boat. After the boat was freed from the ampoule, it was removed and weighed. A total of 82.1 gms of In had evaporated from the boat.

4. CONCLUSIONS

Although all of the ingots grown during the program were polycrystalline, it is clear that the system and the technique would yield single crystals of InP if the problem of oxides floating on the melt surface could be solved. This problem was partially eliminated by hydrogen heat treatment of the indium at 1100°C . There remains the problem of removing the oxygen introduced into the growth ampoule as contamination in the as-received phosphorus.

5. RECOMMENDATIONS

Any further work should address the problem of removing oxides from the phosphorus. The problem of residual indium oxide has been eliminated, but good single crystal growth cannot be achieved with the horizontal gradient freeze technique with an oxide film floating on the melt.

REFERENCES

1. W. P. Allred, Final Report, Contract No. F19628-79-C-0096, "High-Pressure Gradient-Freeze Growth of Single Crystals of Indium Phosphide", 31 Dec 1980.
2. W. P. Allred, Final Report, Contract No. F19628-77-C-0105, "High-Pressure Gradient-Freeze Growth of Single Crystals of Indium Phosphide", Dec. 1978.
3. T.C.Harman, J.I.Genco, W.P.Allred, and H.L.Goering, J. Electrochem.Soc., 105, 731 (1958).
4. G.R.A ntell and D.Effer, J. Electrochem. Soc., 106, 509 (1959).
5. L.R.Weisberg, F.D.Rosi, and P.G.Herbert, in "Properties of Elemental and Compound Semiconductors", pg. 25, edited by H.C. Gatos. Interscience Publishers, New York, N.Y. (1960).
6. K.J.Backmann and E. Buehler, J. Electrochem. Soc., 121, 835 (1974).
7. J.B.Mullin, B.W. Staughan, and W.S.Brickell, J. Phys. Chem. Solids, 26, 782, (1965).

*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 (C³I) 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.