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Safe Removal of Arsenic Dust from Gallium Arsenide Crystal Pullers

FINAL REPORT

October 1st 1994 to March 31st 1995

Grant # 1 R43 OH03220-01

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ORIGINAL

CONTENTS

1.Significant Findings.

Arsenic dust can be removed from a gallium arsenide crystal puller by conversion to arsenic trichloride and subsequent trapping in a dry chemical scrubber.
The chlorine caused severe attack on hot molybdenum components, but these were replaced with alternative, inert materials without affecting the puller's performance.
There was initially some attack upon the stainless steel, the main material of construction of the puller. It was found that this could be prevented by careful removal of water, using vacuum baking.
Attack of the grown crystal occurred. This is significant not because of the loss of material which is not great, but because the gallium chlorides produced remain in the puller.

2.Usefulness of the Findings,

The method greatly reduces the operators exposure to arsenic. The exposure is not completely eliminated as was hoped, because the crystal must be removed from the puller before the chlorination.

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3.Abstract

In the Liquid Encapsulated Czochralski process for the crystal growth of gallium arsenide, finely divided arsenic dust is deposited on the inside walls of the chamber. Between growth runs this dust is removed by operators, who are exposed to this toxic and carcinogenic material. In this program the arsenic dust was converted to arsenic trichloride by reaction with elemental chlorine, removed from the chamber in a flow of inert gas and trapped in a solid state scrubber. Thus the cleaning process was made both safer and less burdensome.

Within the constraints of the Phase 1 program it was demonstrated that arsenic could be successfully removed by this method. Attack occurred on the stainless steel and molbydenum from which the puller and gas lines were constructed,which generated chlorides of chromium, iron and nickel which would be undesirable contaminants in gallium arsenide crystals.This corrosion was suppressed by careful removal of water vapour and by keeping the heater temperature below 500^{o}C.

However, attack on the crystal means that has to be removed before the chlorine transport is carried out.

4.Aims of the Program

To develop a chemical cleaning process for Liquid Encapsulated Czochralski crystal pullers, thus reducing the operators' exposure to arsenic, and improving the economics of the process. The arsenic waste will be collected in an easily disposable form.

5.Background

The growth of the market for microwave and optoelectronic devices has led to an increasing demand for gallium arsenide substrates.These substrates are manufactured at four major vendors in the United States,plus several in-house captive producers. Worldwide there are about twenty - five companies active in this field.

In each case the substrates are produced using the following stages:-

(1) Synthesis of GaAs from the elements.
(2) Crystal Growth
(3) Ingot Anneal
(4) Ingot Grinding (to precise diameter)
(5) Wafering
(6) Polishing

In some plants a further step, epitaxy, is also carried out.

In each of these stages there is some exposure of the operators to arsenic,gallium, and possibly arsine .
The toxicity of inorganic arsenic has long been known.(Arsenious oxide was a favourite poison in Victorian times).More recently arsenic has been determined by NIOSH to be a carcinogen[1-3]. Gallium arsenide has been shown to dissociate and produce free arsenic in animals, and must therefore also be treated as a potential occupational carcinogen[2]. GaAs exposure may also result in pulmonary fibrosis[4].
J.W.Sheehy and J.H.Jones[5] published an account of arsenic exposures and controls in three GaAs production units. Exposure of operators to arsenic varied from plant to plant. In one plant,in all processes except epitaxy, average arsenic exposures were at or above the OSHA action level of 5 micrograms/m^3.
Although highest contamination levels were found in the various production areas, arsenic was also detected, at average concentrations of 1.4 micrograms/m^3, in breakrooms and offices 20 to 60 ft from the production areas.
Apart from the health hazard, this general contamination leads to major expense if a GaAs plant is later to be converted to other uses. For example, when Spectrum Technology closed in 1989, clean-up of the buildings took six -nine months involving major costs.

Another major concern is that Sheehy and Jones[5] found that a significant part of the arsenic detected passed through their filters (0.8 micrometer pore size) and was trapped in charcoal tubes. This suggests that some of the arsenic is in the vapour state, possibly as arsine formed by the reaction of arsenic dust with moisture.

These results suggest that for both economic and health reasons, efforts should be made to contain the arsenic, reducing operators exposure and contamination of the buildings. Jones and Sheehy found that the highest levels of contamination occurred in the LEC process, particularly during cleaning, as shonwn in Table 1 (their Table IV)

TABLE 1. Total Arsenic Concentration during LEC Cleaning

Plant #	Sample type	No. of samples	Average sample duration min.	Arsenic Concentration[a] Arithmetic Mean (g/m^3)	Geometric Mean (g/m^3)	Range (g/m^3)
1	Personal[a]	5	71	1070	760	250-2700
	Personal[b]	5	79	12	11	6.9-19
	Area-LEC	10	279	4.0	3.6	1.3-7.5
2	Personal	4	177	430	300	125-1030
	Area-LEC	4	186	58	51	26-107
	Area-Control Panel[d]	3	202	<0.8	<0.7	<0.4-<1.2
3	Personal	3	60	0.8	0.6	0.3-1.4
	Area-LEC	6	62	1.0	0.9	<0.6-1.7

a Sum of arsenic collected on filter and charcoal tubes
b Supplied air respirator worn by operator who is cleaning
c Air purifying respirator worn by operator who is not cleaning
d The control panel outside the LEC puller room.

In this approach the arsenic can be completely confined within the puller and an absorption column, giving effectively zero operator exposure at this stage, and yielding waste arsenic in a form easily handled and disposed of.

The growth of gallium arsenide crystals by the Liquid Encapsulated Czochralski(LEC) process is carried out either by a High Pressure(300 psi) or Low Pressure process.(25 psi)

In the High Pressure Process the following stages occur:-

(i)Gallium metal, Arsenic and boric oxide are loaded into a Pyrolytic Boron Nitride crucible and placed in the pressure chamber of the puller.

(ii) The chamber is purged and pressurised with argon and the charge is then heated until reaction takes place between the elements to form gallium arsenide, which is then melted. The boric oxide, as a molten glass, encapsulates the charge to prevent loss of arsenic.
During the synthesis the pressure in the chamber reaches 900 psi. and is afterwards reduced to 300 psi. which is then maintained throughout the growth process.

(iii) A single crystal seed crystal is brought into contact with the melt and crystal growth carried out.

(iv) The puller is cooled to room temperature and the crystal removed.

(v) The puller is cleaned in preparation for the next run.

(vi) Finally the graphite insulation package is heated in the puller under vacuum to remove absorbed air and water vapour.

In the low pressure process, the synthesis is carried out as a separate operation, and the charge consists of polycrystalline gallium arsenide and boric oxide. Crystal growth is carried out at a pressure of 25-30 psi.

In both processes, and despite the presence of the boric oxide encapsulant, some arsenic is lost from the melt and deposited as a fine powder on the inside walls of the chamber and on the graphite insulation. For example, in the growth of an eight kilogram GaAs crystal in the Cambridge Instruments CI 358 puller, the arsenic loss is typically 130gm +/-5gm..
This powder is highly toxic and carcinogenic and in order to clean the puller safely the operators wear full cover disposable clothing, and positive feed breathing apparatus. The cleaning process produces a considerable quantity of contaminated clothing and cleaning materials which must be disposed of as toxic waste. In addition, depending on the efficiency of the exhaust system, there is likely to be contamination of the puller environment.
The cleaning operation takes two to four hours, is understandably unpopular with operators, making it difficult to retain experienced employees in this position.

In the proposed process the arsenic dust in the puller at the end of the crystal growth run is transferred chemically

to an absorption column from which it can be safely removed. This will make the cleaning process as practised at present, completely unnecessary.

The advantages of this process will be:-

(1) Reduced exposure of operators
(2) Reduction in volume of toxic waste
(3) Improved life of insulation
(3) Reduced contamination of premises (with subsequent cost savings)
(4) Improved job satisfaction, making it easier to retain experienced employees.

6.Experimental design and Methods

6.1.General Principle

The intention is to develop a system in which the arsenic is transferred from the puller to a safe container without opening the puller, and hence without releasing arsenic dust into the atmosphere. The method proposed is to convert the arsenic to arsenic trichloride which is highly volatile and can be carried off in a stream of gas into a suitable scrubber.

6.2Modifications to the Puller

The growth chamber of the Cambridge 358 puller which was used for this program,is shown schematically in Figure 1 and contains the following materials:-

Chamber walls,base and top plates - water cooled stainless steel. The walls of the chamber have a thin (1/8/inch) liner covering a helical cooling channel.
Graphite heater
Graphite insulation - alternate layers of solid graphite and felt, a total of 24 pieces.
Outer crystal pull rod - stainless steel
Inner crystal pull rod - molybdenum
Seed chuck - molybdenum
Crucible lift rod - stainless steel
Crucible support - graphite.
Thermocouple - W,Re5%/W,Re26% in molybdenum sheath,

At the end of a crystal growth run arsenic dust is deposited on the top graphite, the exposed walls and the lower heat shields. Because of the nature of the construction, some arsenic dust penetrates between the layers of insulation. It is therefore common practice on opening the puller after a run, to remove most of the loose dust with an industrial HEPA filter vacuum cleaner. All of the graphite parts are then removed and individually cleaned by wiping or

scrubbing. It is during this process that the major exposure to arsenic occurs.

In addition it is essential between each run to adjust the crucible support system so that the crucible runs centrally on the puller axis. This would necessitate removal of all the graphite even if this were not necessary for cleaning.

To simplify this process it was intended to replace the existing graphite insulation with a four piece 'fiberform' insulation, giving minimal surface area and no penetration of arsenic into the shielding.
The crucible lift and rotate system was replaced with a simpler one inch rod, which does not need adjustment between runs.Hence if the chlorine cleaning process is successful, it will not be necessary to remove the insulation between runs. This will lead to further economies since the main cause of wear to the insulation is damage during removal from and replacement in the puller.

6.3.Conversion of Arsenic to Arsenic Trichloride

The chosen method should attack the arsenic rather than the crystal and not corrode the materials of construction of the puller. Graphite is inert to chlorine. In fact the standard method of purifying graphite before use in crystal pullers is to treat it in chlorine at 2000^{o}C.
The other materials form stable chlorides as can be seen from the Gibbs Free Energy Plots in Figure 2. We therefore have to find a means of preferentially attacking the arsenic.
The physical nature of the material is in our favour; since the arsenic is a finely divided powder, its reaction rate is likely to be much higher than of the massive materials.

J.R.Partington[6] stated that arsenic is spontaneously inflammable in chlorine, "even when the elements are dry". K.Orlanger who participated in the plasma work described below[7], found that arsenic is readily converted to chlorine at temperatures of 250-300^{o}C. It seems likely therefore that admitting chlorine to the puller at the end of a run will convert the arsenic to $AsCl_3$, which can be flushed out. Table 2 shows the vapour pressure of $AsCl_3$ as a function of temperature.

Table 2 Vapour Pressure of Arsenic Trichloride

Vapour Pressure mmHg	1	10	40	100	400	760
Temperature oC	-11.4	23.5	50.0	70.9	109.7	130.4

There are two possible disadvantages to this approach.
(1) The yield of high quality, single crystal gallium arsenide is strongly dependent on the thermal environment of

the puller. In spite of considerable effort in recent years to model thermal distributions in crystal growth, all practical puller systems in manufacturing use have been arrived at pragmatically, by a system of trial and error plus years of experience. Pullers users are therefore reluctant to change their established thermal geometry without clear evidence that yields will be maintained.
Therefore, it must be demonstrated that not only will the arsenic removal system work, but the growth of good quality single crystals is not impaired by the modified geometry.
(2)It may not be possible to remove all the arsenic without some attack on the chamber materials.

6.4.Collection of Arsenic Trichloride

The halides formed during chlorination will be entrained in argon and collected in a suitable scrubber. Final traces will be removed by vacuum baking.
Analysis of the wall deposits in LEC pullers by Rumsby and Ware[9] have shown them to consist of 95-98% As plus small quantities of B_2O_3 and gallium. The latter is present on the walls as oxide, but is also occasionally found on parts of the graphite as gallium metal. Hence the material absorbed in the scrubber will consist mainly of $AsCl_3$ with minor quantities of BCl_3 and $GaCl_3$. Also there may be traces of Fe,Ni,Cr and Mo chlorides.

7.Research Program

It was intended to carry out the research program in the following stages :-

(1)Obtain and fit improved graphite system to puller.

(2)Obtain and fit improved crucible lift and rotate system

(3)Carry out GaAs growth run to check on effect of puller modifications changes on growth conditions.

(4)Fit chlorine handling system and scrubber.

(5)Carry out a series of experiments at different chlorine/argon flow rates and pressures , and puller temperatures to determine optimum conditions to give effective cleaning in the shortest possible time.

7.1.Results.

This section contains a detailed description of the experiments performed and the results obtained.

7.1.1.Base Line Growth run

For over eighteen months before the start of this program the puller had not been used for growth of standard gallium arsenide crystals, but instead for the growth of ternary $In_xGa_{1-x}As$ crystals. A standard 4kg/ 2inch diameter GaAs crystal was therefore grown to give a base line against which to assess the results of the puller modifications. This run was successful, a completely single crystal of good diameter control was obtained.

7.1.2.Puller Modifications.

It was impossible to test the improved insulation. Although it was ordered as soon as the contract was awarded, against a promise of 6-8 weeks delivery, it was not in fact delivered until two weeks before the end of the six months contract period and then was so faulty it had to be returned to the manufacturer.
However, a similar system has been tested at a major GaAs manufacturor and found satisfactory as far as crystal growth is concerned.

The complicated crucible support system which is standard with the Cambridge 358 puller was replaced with a simple water cooled molybdenum rod, connected to the crucible support by a cone and socket joint. This is a major improvement on the standard system, without loss of single crystal yield.

7.1.3.Puller cleaning Run PC-1

A standard 4 kg/ 2 inch diameter crystal was grown. At the end of the run the heater temperature was reduced to 195°C, the pressure reduced to 5 psi above atmospheric and the system allowed to stabilise.
A flow of argon at 2 l/min was established through the puller and the scrubber. Then the chlorine flow was initiated and the combined flows set at 1 l/min Cl_2 and 1 l/min argon. This was maintained for two hours, after which the chlorine was shut off, the argon increased to 2 l/min and the system flushed with argon for 12 hours.

The CI 358 puller controls crystal diameter by monitoring weight, hence the crystal is supported by a load cell giving a continous readout of crystal weight. During the course of the chlorination the crystal lost a total of 14 g.

After cooling to room temperature, the puller was opened and examined.

A small amount of white fumes were seen, which smelt strongly of HCl. Some arsenic powder still remained on the top graphite. The inside walls of the chamber showed flow

marks as if a liquid had been refluxing and there was a black tarry, fuming deposit on the base plate.
The fumes observed were probably due to hydrolysis of $AsCl_3$ and/or $GaCl_3$.
Samples of the deposits were removed for analysis and found to contain a mixture of Fe,Cr,Ni,As, and Ga chlorides.
The crystal and crucible were removed,and the chamber was closed, evacuated, backfilled with argon at 50 psi and heated to 610°C (heater temperature)
Then the pressure was reduced to 6 psi, the temperature set at 610°C, and the chlorination repeated. The temperature of the chamber cooling water was increased from 26 to 36°C to reduce condensation on the walls.

After cooling the puller was opened and it was found that there was a fairly heavy deposit of molybdenum chlorides plus some chromium chloride. There had been severe corrosion of the thermocouple sheath and the molybdenum bolts on the heater lead throughs. The crucible support rod (also Mo) was not attacked presumably since it is water cooled; nor was the molybdenum inner pull rod.

7.1.4.Puller Cleaning Run PC-2

The puller was cleaned,the molybdenum bolts replaced with graphite bolts and the Mo thermocouple sheath by alumina.
The system was then vacuum baked. Deposits of Mo, Fe As and Cl were found. These must have come from within the graphite insulation. The puller was therefore vacuum baked for four periods of five hours, until no further deposits occurred.

Next the chlorination process was repeated without crystal growth and with a heater temperature of 365°C.

Finally the system was vacuum baked at 360-460°C for 2.5 hours.
Upon cooling and opening the puller it was found to be clean with no deposits on the graphite or the puller walls.

Thus it seems that provided the heater temperature is kept below 500°C there is little or no attack on the puller materials.

7.1.5.Removal of Arsenic in absence of Crystal.

The purpose of this run was to see if arsenic could be removed from the puller if the crystal was not present without attack on the puller or supply lines.

45g of As were loaded into an otherwise empty crucible which was placed in the puller. After evacuation and backfilling

with argon the heater temperature was raised to 1120°C to evaporate the arsenic from the crucible to the insulation and the chamber walls, thus simulating a growth run.

Next the puller was cooled to a heater temperature of 360°C and chlorination carried out as before. (0.5 l/min Cl_2 and 1.5l/min Ar for 2 hours).

The puller was flushed with Ar for 23 hrs at 1.5 l/min and vacuum baked at 460°C.

On opening the puller it was found that all the arsenic had been removed. There was a very slight yellow deposit on the base plate which proved to be insufficient to obtain analytical samples.

7.1.6. Crystal Growth and Puller Cleaning

A standard 4 kg/ 2 inch gallium arsenide crystal was grown. After the crystal was lifted its maximum position, the heater temperature was reduced to 360°C and the pressure to 5 psi.

During chlorination the heater temperature was held in the range 360-390°C. The gas flow was 0.5 l/min Cl_2 and 1.5 l/min Ar.

The crystal was attacked by the chlorine losing 96 gram and eventually falling from the seed holder, presumably due to thinning of the 'neck' by the chlorine. After chlorination the puller was flushed with argon as before.

On opening the puller it was found to coated with a fairly heavy deposit mainly of gallium chloride, which is less volatile than arsenic trichloride.

7.1.7.Trapping of arsenic trichloride.

The effluent gases were passed through a Novapure dry chemical scrubber, designed to trap the arsenic trichloride, other likely chlorides and excess chlorine.

The scrubber consists of a column of resin pellets in a disposable canister. The model employed contains 20 gallons of resin,sufficient for ten typical growth runs. A detector may be fitted to indicate when the column is full. At this point the canister can be changed for a fresh one, the full one sealed and removed from the puller area. Thus there is no need to handle thw arsenic residues.

The scrubber performed as specified and absorbed all the halides produced in this program.

8.Discussion and Conclusions.

The results obtained suggested that provided precautions were taken to remove residual moisture from the insulation by vacuum baking and to keep the heater temperature below 500°C, arsenic could be successfully removed from the puller

without attack on the stainless steel components. Formation of molybdenum chlorides was avoided by replacement of molybdenum parts by inert materials(graphite and alumina). Chlorine attack on the crystal occurred even when it was raised to the highest possible position.
The process must therefore be operated by removing crystal and crucible before chlorine transport of the arsenic. Thus it seems likely that the major exposure to arsenic can be avoided, but that some exposure is inevitable during removal of the crystal.

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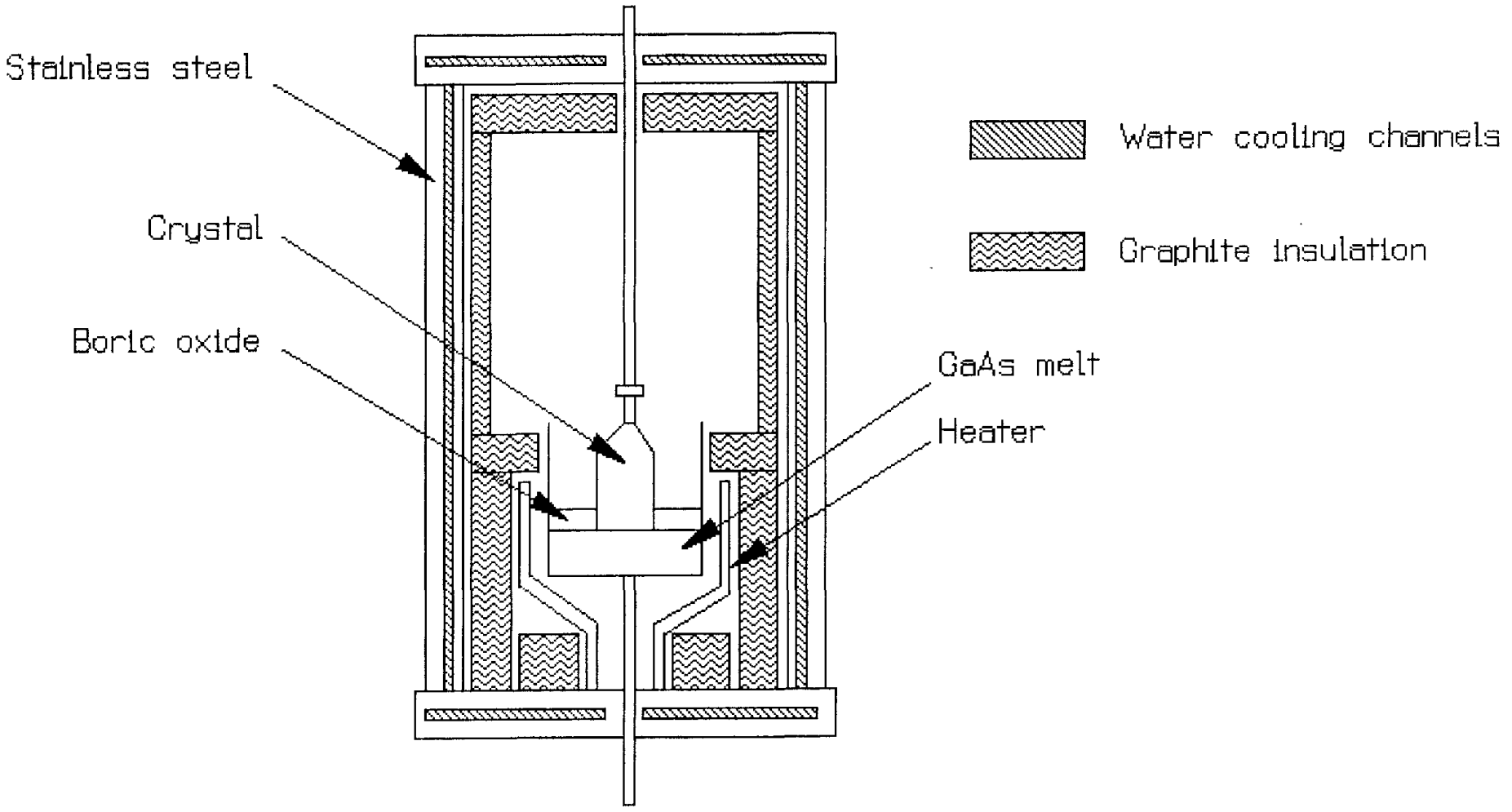
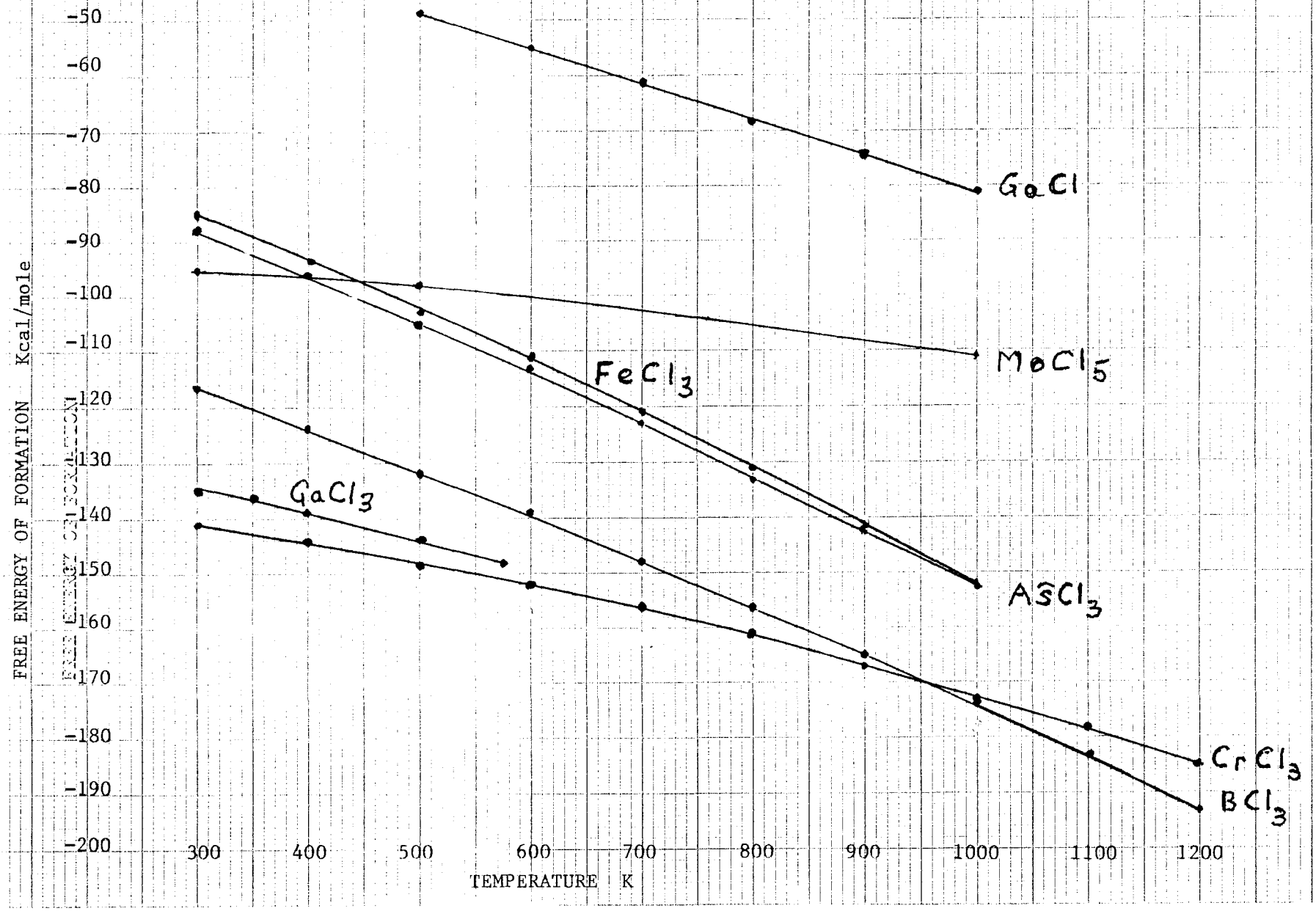
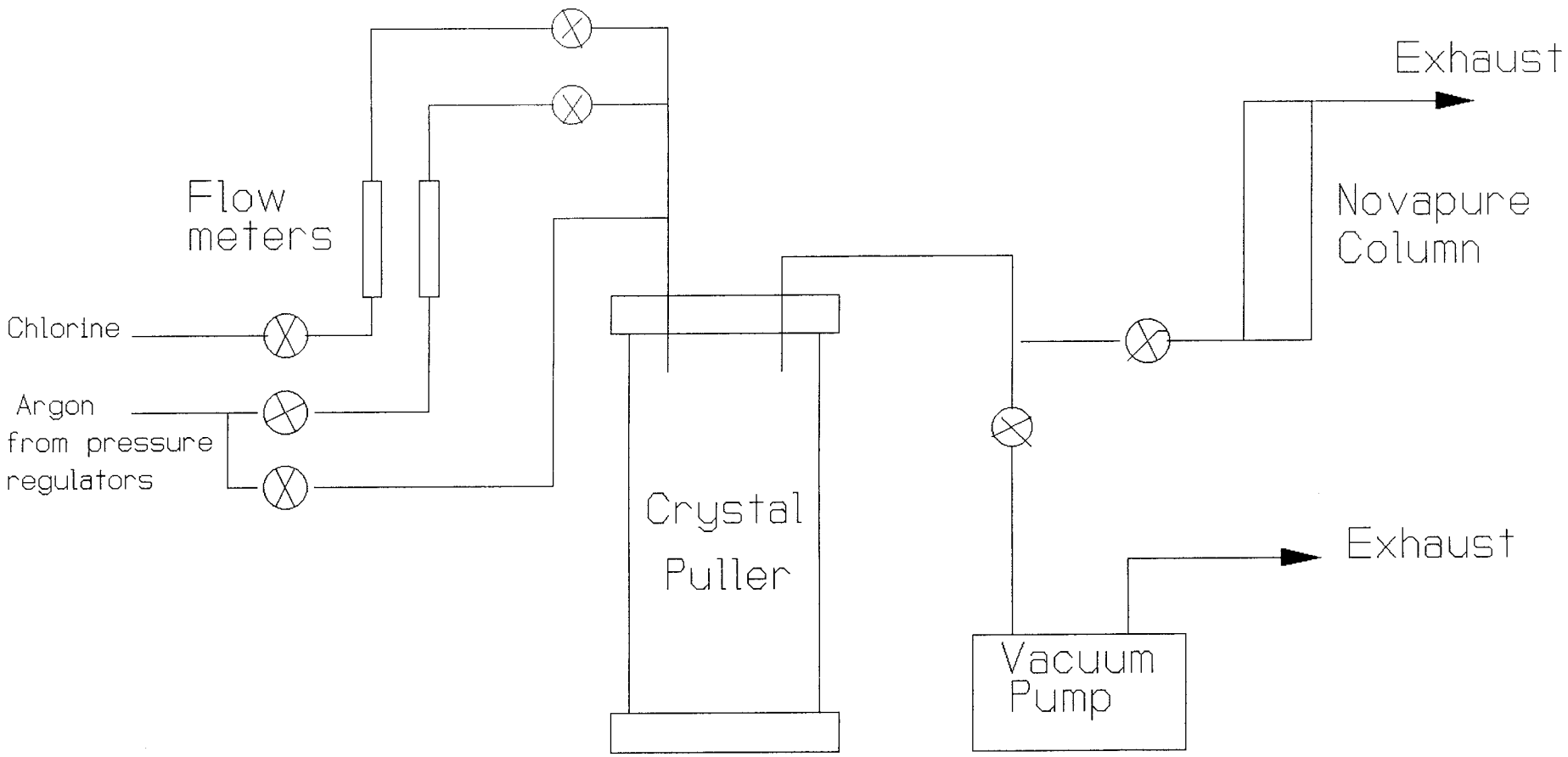


Figure 1 358 Puller- Schematic

Figure 2 Free Energy of Formation of Chlorides of Puller Materials





Puller Cleaning System

Ware Technical Services Inc.

Figure 3

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15. Supplementary Notes

16. Abstract (Limit: 200 words) A chemical cleaning process was developed for liquid encapsulated Czochralski crystal pullers which would reduce the exposure of the operators to arsenic (7440382). In this process the arsenic would be transferred from the puller to a container without releasing arsenic dust into the atmosphere. The arsenic could be converted to arsenic-trichloride which will be carried off in a stream of argon gas into a suitable scrubber. Provided precautions were taken to remove residual moisture from the insulation by vacuum baking and keeping the heater temperature below 500 degrees-C, arsenic could be successfully removed from the puller without any attack on the stainless steel components. Molybdenum-chloride formation was avoided by replacement of molybdenum parts by inert materials such as graphite and alumina. Chloride attack on the crystal occurred even when it was raised to the highest possible position. The authors suggest that the process must be operated by removing crystal and crucible before chlorine transport of the arsenic. While the major exposure to arsenic could be avoided, it appears that some exposure is inevitable during removal of the crystal.

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