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Mass Spectrometric Studies of Impurities in Gallium Arsenide Crystals

J. C. BRICE, J. A. ROBERTS, G. SMITH
Mullard Research Laboratories, Redhill, Surrey, UK

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Techniques for the investigation of impurities in gallium arsenide crystals using mass spectrometry are described. The results obtained show a fair correlation with electrical measurements. Flat-bottomed etch pits are found which can be correlated with the oxygen content.

The use of silica, boron nitride, alumina, and vitreous carbon crucibles is shown to contaminate the crystals. For crystals grown from silica crucibles, the silicon content decreases rapidly with increasing arsenic pressure during growth. From the distribution of impurities along the lengths of crystals, a number of distribution coefficients have been estimated.

1. Introduction

The use of the AEI MS7 spark-source mass spectrometer for trace impurity analysis of solids is well known [1, 2] and its use to determine impurity levels in semiconductors has also been described [3 - 5]. This paper describes some techniques for the analysis of gallium arsenide which have not been reported but seem to be of general interest. The results cast some light on the conditions necessary to minimise contamination during crystal growth. The crystals examined were grown either by the Bridgman method [6] or in a syringe puller [7].

For the type of work described, the MS7 instrument has the advantages of high sensitivity and a simultaneous coverage with approximately equal sensitivity for all the elements. The 500 kHz radio-frequency spark source avoids local heating but produces an ion beam with a large energy spread. This requires the use of a double-focusing spectrometer of the Mattauch-Herzog geometry [8, 9] to bring ions of all masses into focus in one plane where the spectrum may be recorded on a photographic plate.

The sample is usually prepared in the form of two rod electrodes about 1 cm long with a cross-sectional area of approximately 2 mm^2. They are mounted horizontally opposed in the ion-source chamber and are adjustable in all three directions by external controls. The small gap between the electrode tips is adjusted in line with the spectrometer axis, and a pulsed radio-frequency voltage which is variable in repetition rate, pulse length, and amplitude up to 80 kV is applied. A spark passing between the electrode tips produces positive ions from the sample. These ions are then accelerated through a system of slits by a potential difference of 20 kV before passing through the analysers. The integrated ion-beam current measuring the exposure of the photographic plate is determined from a monitor electrode which intercepts 50% of the ion beam before dispersion of the ions in the magnetic analyser. The plate is moved horizontally across the magnetic analyser gap to give fifteen successive graded exposures of the complete mass spectrum on the one plate. The exposures are usually increased by a factor of three between steps giving a range of 10^7 to 1. The sensitivity is such that an isotope corresponding to 1 in 10^9 or 0.001 ppm (atomic) of the major constituent is detectable on the longest exposure if free of interferences by other isotopes.

2. Techniques

2.1. Sample Preparation

Electrodes at least 1 cm long and 1.5 mm square were found to be satisfactory for most samples.

However, for high-resistivity material, shorter electrodes of smaller cross-section (e.g. 1 mm square) were found to be more useful. Because of the possibility of impurities plating onto the sample, aqueous acid etchants were not used for the final etch. It was however necessary to have a vigorous etch to remove material used for mounting the specimens during cutting. Preliminary measurements showed impurities from this source. The following procedure was found to be satisfactory: (i) degrease in methanol; (ii) wash with water; (iii) etch for 1 min in aqua regia; (iv) wash with water; (v) etch for 2 min in a 10% bromine in methanol solution (to remove plated impurities and chloride ions from the surface); (vi) wash thoroughly in methanol; (vii) dry under an infrared lamp.

All reagents used for cleaning were of the highest purity, electronic grade where available, and great care was taken when handling samples: PTFE tipped tweezers were used and nylon gloves were worn by the operator for source assembly.

2.2. Presentation of the Sample

Routine mass spectrographic analysis with frequent interchange of sample electrodes always produces results for carbon, oxygen, and nitrogen not less than the 10 to 100 ppm level, owing to the residual gases. As carbon and oxygen are important impurities in gallium arsenide, an attempt was made to achieve a low, and reproducible, blank contribution for these elements. To reduce the contribution from adsorbed surface layers and residual gases in the source unit, the source was baked out overnight, with the sample in position before each analysis. This gave a reproducible, initial source pressure of 5×10^{-8} torr, but this rose rapidly after sparking was commenced to the 5×10^{-7} torr region owing to the volatilisation of arsenic.

It is impossible in the absence of gallium arsenide free from carbon and oxygen to determine a true blank, but with this procedure the lowest recorded figures were 0.3 ppm for carbon and 0.1 ppm for oxygen and nitrogen. In the light of this evidence, we felt justified in accepting values obtained for these elements to the nearest 1 ppm.

It was found that the additive effect of high spark voltage, high pulse repetition rate, and long pulse length caused overheating in the electrodes and rapid volatilisation of the sample in the spark region. The highest beam currents without these abnormal effects were obtained with a spark voltage of 25 kV, a pulse repetition rate of 300/sec, and a pulse length of 200 μsec. The electrodes still eroded away more quickly than with metallic samples, making frequent spark gap adjustment necessary. Some analyses were made on high-resistivity gallium arsenide and with these samples it was necessary to operate with a spark voltage of 40 kV to induce sparking.

The maximum exposures made were 1 μC at the monitor collector to give approximately 1 in 10^9 sensitivity for each isotope. Previous workers have reported a time of 30 min for this exposure, but we found that it took 2 h including the time taken for spark gap adjustment and alignment during the exposure. Any attempt to increase the rate of the exposure resulted in increased halation on the photographic plate around the major isotope lines, causing higher limits of detection in this region.

The magnet current was set to about 210 mA to give a recorded mass-number range from 5 to 215 covering elements from lithium to bismuth. An entrance slit of 0.002 in. (1.0 in. = 25.4 mm) was used which gave a resolution of 1200 at mass number 31 and 2800 at mass number 207.

3. Interpretation of Spectra

The elements present were identified from the relative position of the lines recorded in the mass spectra by: (i) the mass number of the isotopes; (ii) the isotopic abundance pattern; and (iii) the presence of the multiply charged ions. Because impurity concentrations were low, relatively few lines were produced, making identification from isotopic abundance patterns difficult in many cases. The low spark voltages used made the relative intensity of lines due to the multiply charged ions low, and although this reduced spectral interference it made the confirmation of impurity identity more difficult.

Quantitative estimation was made visually from the exposure level, which gave a just-detectable line for a given isotope. This method of interpretation is rapid and suitable for this type of survey analysis. The relative sensitivities of the elements were assumed to be equal. This is not accurate, but is generally accepted to be so within a factor of 3 for most elements. The purpose of most of this work was to make comparisons of the purity of different samples, and therefore quantitative accuracy was not as important as the precision of the results.

It will be seen on reference to table I that not all the elements of the periodic table have been included. All elements were looked for, and the table includes all those found, plus the ones considered to be significant impurity elements if they had been present. For quantitative purposes, the line due to the major isotope was used whenever possible, but about one-half of the elements listed were estimated on the one-half or one-third mass numbers. Nine of these multiple charge lines were chosen, because "halation" on the plate around gallium ($^{69}Ga^+$, $^{71}Ga^+$) and arsenic ($^{75}As^+$) made the fractional mass numbers more sensitive. The remainder were chosen because interference was possible from other lines which would not have been resolved on the plate. These multiply charged ion lines gave a reduced sensitivity and a factor had to be calculated and introduced. With a spark voltage of 25 to 30 kV, the factor was approximately 10 for each degree of ionisation. With a spark voltage of 40 kV, the factor was found to be 5.

TABLE I

Element	Line used for estimate	Detection limit (ppm atomic)
Bi	104½	0.01
Pb	208	0.002
Hg	202	0.004
Au	98½	0.01
W	184	0.004
Ba	136	0.01
Cs	133	0.003
I	127	0.01
Te	130	0.01
Sb	121	0.006
Sn	120	0.01
In	115	0.003
Cd	56½	0.1
Ag	53½	0.02
Br	40½	0.06
Se	40	0.2
Ge	24⅔	0.1
Zn	21⅓	0.6
Cu	31½	0.02
Ni	19⅓	0.1
Co	29½	0.01
Fe	56	0.01
Mn	55	0.001
Cr	52	0.01
Ca	20	0.01
K	19½	0.01
Cl	35	0.002
S	10⅔	0.2
P	15½	0.01
Si	14½	0.1
Al	13½	0.01
Mg	24	0.01
Na	11½	1
F	9½	0.02
B	11	0.002
Li	7	0.01
		Lowest detected levels (ppm)
C	12	0.3
N	14	0.1
O	16	0.1

4. Results and Discussion

A number of specimens were analysed from crystals grown both in a Bridgman apparatus from silica crucibles [6] and in a syringe puller [7] with a boron nitride-silica seal using vitreous carbon, alumina, or boron nitride crucibles. The boron nitride crucibles were used with vitreous carbon susceptors. The other materials were used alone.

Table II gives some typical analyses and shows that there are small quantities of many elements in all the crystals. Table III gives the detection limits of elements not detected. Of the impurities occurring at high concentrations, the most consistent are Cl, C, O, and N. The first two of these probably are present to some extent in the starting materials as a consequence of the methods of preparation, and the last two are probably introduced during subsequent handling. The copper concentrations were consistently low; usually below the limit of detection, 0.02 ppm. This suggests that much larger values reported by other workers may arise from contamination, on the sample surface during etching or grinding, for example.

It is possible to correlate the mass spectra directly with electrical measurements of the number of excess carriers (obtained using the van der Pauw method [10]) only when one impurity is dominant. On fig. 1a, the results of doing this are represented and it can be seen that a very good correlation exists. More indirectly, using carrier density and mobility, it is possible to calculate the total number of "ionised impurities" from curves given by Weisberg *et al* [11]. The points shown as O and Δ on fig. 1a are the results of doing this when the concentrations of C, O, and N are omitted from the mass spectral analyses. The results of including the C, O, and N are shown on fig. 1b for the points marked Δ on fig. 1a. From this data, it

TABLE II

Impurity[a]	Bridgman crystals		Pulled crystals			
	C41	C46	C67[b]	EB56	EB58	EB79
Fe	0.03	0.01	0.1	0.1	0.01	0.03
Cr	<0.01	<0.01	1.0	0.1	<0.01	0.03
Ca	0.01	0.1	0.1	0.1	0.01	0.03
K	0.1	0.04	<0.01	<0.02	0.01	<0.01
Cl	0.1	0.1	1.3	13	4	0.1
S	<0.1	<0.1	0.05	<0.2	0.1	1.0
P	<0.01	<0.01	0.01	<0.02	<0.01	<0.01
Si	0.1	2	<0.1	<0.2	<0.1	0.3
Al	<0.01	0.06	0.015	1.0	1.0	<0.01
F	0.06	<0.02	<0.01	<0.04	<0.02	0.06
B	<0.002	<0.002	0.002	<0.04	0.002	0.002
Li	<0.01	<0.01	<0.01	<0.02	<0.01	0.02
C	1.0	1.0	30	30	30	100
N	0.3	0.3	3	3	10	10
O	3.0	1.0	10	10	30	30

(a) Other elements not generally detected in these samples, but small amount of Pb, W, I, Sb, Sn, Cu, Co, Mn, and Mg were detected in some specimens.
(b) Cr deliberately added.

TABLE III

Detection limits of elements not found			
Bi	0.01	Cs	0.01
Pb	0.02	I	0.01
Tl	0.02	Te	0.03
Hg	0.03	Sb	0.05
Au	0.01	Sn	0.03
Pt	0.03	In	0.01
Ir	0.02	Cd	0.03
Os	0.02	Ag	0.02
Re	0.02	Pd	0.04
Ta	1	Rh	0.1
Hf	0.2	Ru	0.03
Lu	0.1	Zr	0.1
Yb	0.6	Sr	0.1
Tm	0.01	Rb	0.01
Er	0.03	Br	0.2
Ho	0.1	Se	0.01
Dy	0.04	Ge	2.0
Tb	0.01	Ga	1.0
Gd	0.6	Co	0.1
Ba	0.01	Sc	0.1

seems that C, O, and N are not fully ionised. In making the indirect comparison, it must be remembered that dislocations may act as scattering centres and that vacancies are electrically active [12], although the number of centres associated with vacancies is small, probably $< 10^{16}/\text{cm}^3$ [13].

Metallographic examination of the gallium (111) faces of crystals* showed a number of flat-bottomed pits. Fig. 2 shows these pits, marked B, which lack the sharp point of the normal dislocation pits, marked A. The number of flat-bottomed pits can be correlated with the oxygen content (see table IV). These pits are probably similar to pits found in germanium, which have been correlated with oxygen and vacancy concentrations [14].

By considering the crucibles from which the crystals were grown, it is possible to obtain some information about contamination due to crucible materials. Table V compares the concentrations of likely contaminants. From this table, it appears that all the materials used could contaminate the crystals. It was found that, in the case of crystals grown in silica boats by the Bridgman technique, the amount of contamination varied with the arsenic pressure present in the ampoule during growth. The rapid decrease

TABLE IV

Flat-bottomed pit density (cm^{-2})	Oxygen content (ppm atomic)
0	1
400	3
800	10
1200	10
2000	30

*Using an etch with a volume ratio of 2 water, 1 nitric acid, and 1 hydrochloric acid, after grinding with 15 μm alumina, and polishing with a 2 water, 3 nitric acid, and 1 hydrofluoric acid mixture.

found is shown on fig. 3 and suggests that the effect is due to attack by gallium on the boat: the activity of the gallium will decrease rapidly with increasing arsenic pressure.

When more than one specimen per crystal is analysed, it is possible, knowing the positions of the specimens, to estimate the distribution coefficients of the various impurities from the normal freezing equation. In the case of volatile solutes, the value obtained will possibly be

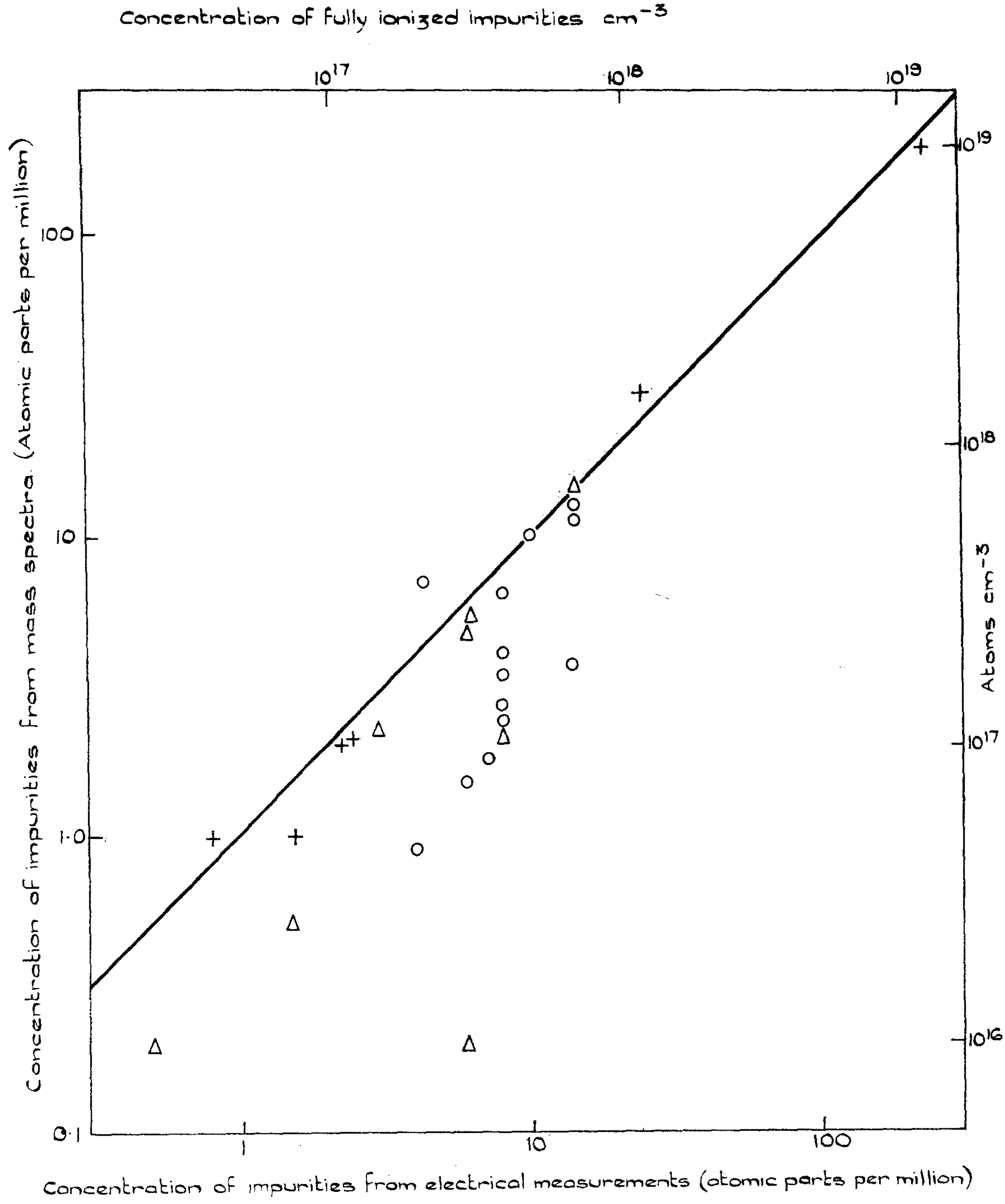

Figure 1a Concentrations of impurities from mass spectra (excluding C, O, and N) versus those from electrical measurements: +, crystals with one dominant impurity: O, Δ, indirect calculation of ionised impurity density.

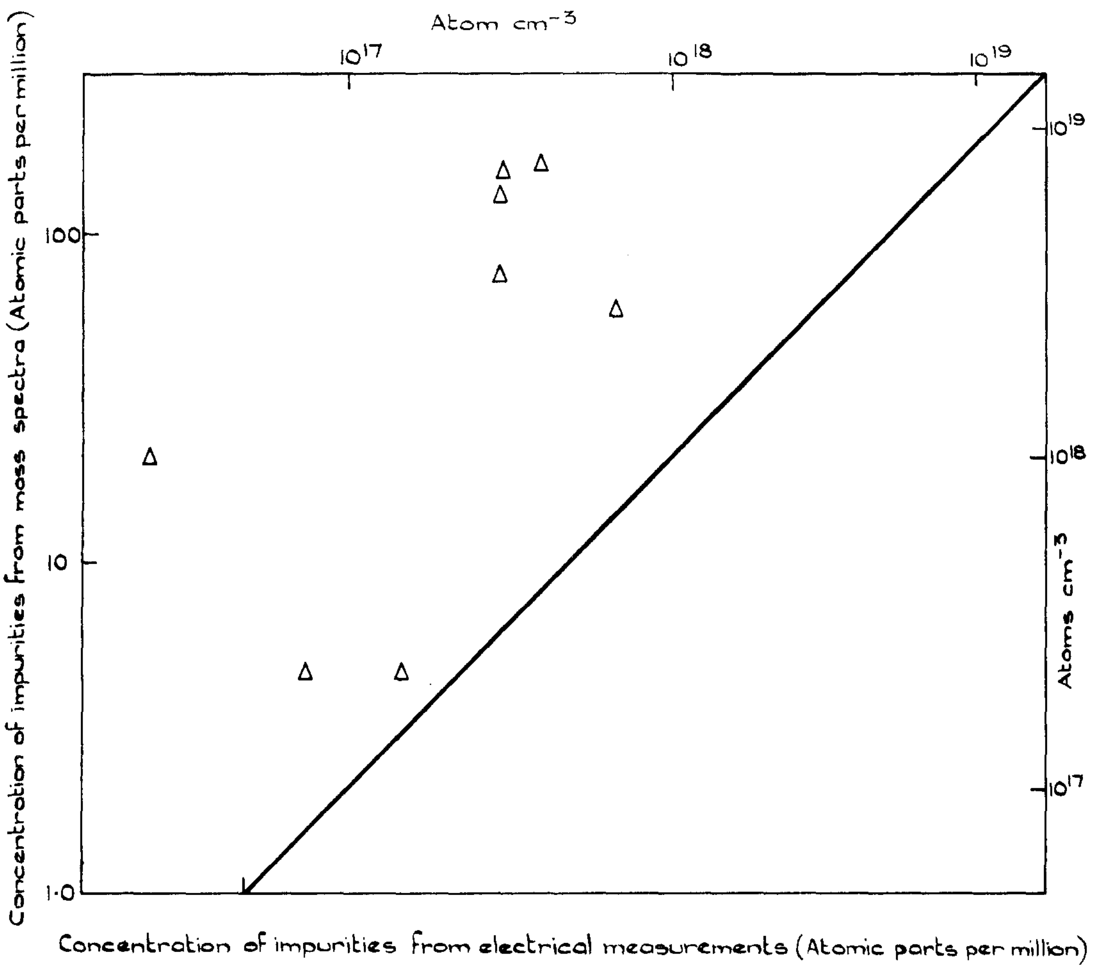

Figure 1b Results for points marked Δ in fig. 1a if concentrations of C, O, and N are included. The lines drawn are those for a one-to-one correlation of the results.

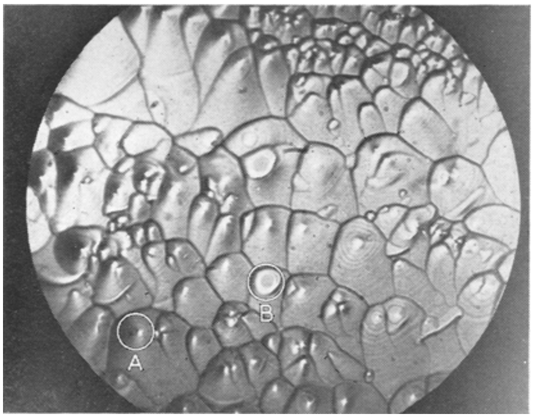

Figure 2 Dislocation (A) and shallow pits (B) on gallium arsenide (111) face.

affected by the partial pressure of the volatile component in the vapour phase. The effect of exchange reactions between the vapour and the liquid will be such as to give a distribution coefficient between the equilibrium value and 1. The values obtained are shown in table VI and it can be seen that agreement between the values found by this method and others is reasonable.

5. Conclusions

From the work described, it can be seen that mass spectrometric studies can be useful in evaluating the factors controlling the purity of crystals of semiconducting compounds, such as gallium arsenide, grown from the melt.

The concentration of impurities in gallium arsenide determined by mass spectrometry can

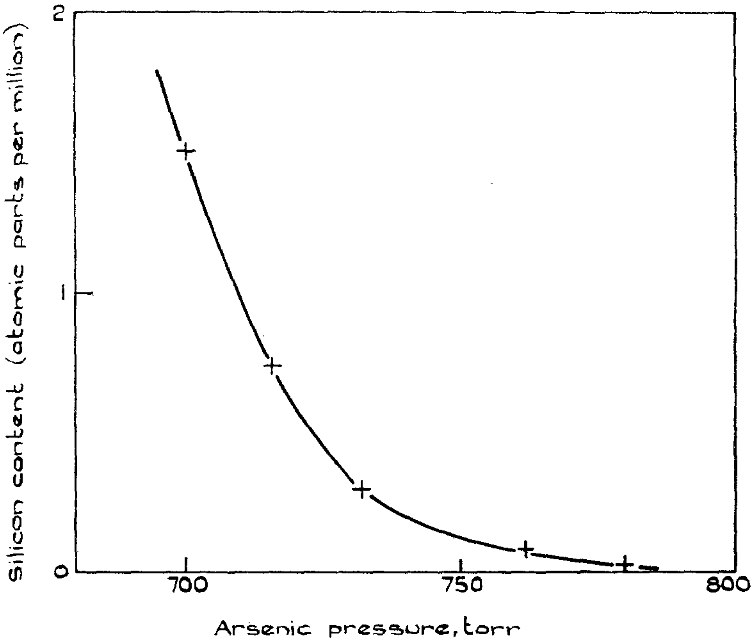

Figure 3 Average silicon content as a function of arsenic pressure.

TABLE V

Crucible material	Impurity concentration (ppm atomic)					
	C	N(e)	O(e)	B	Al	Si
Silica(a)	6	1	3	<0.002	0.02	0.01-2(d)
Vitreous carbon(b)	50	2	16	<0.002	0.1	0.05
Alumina(b)	30	6	20	<0.002	1	<0.1
Boron nitride(b, c)	100	10	30	0.002	<0.01	<0.01

(a) Bridgman grown.
(b) From syringe puller.
(c) In a vitreous carbon susceptor.
(d) See text and fig. 2.
(e) The difference in the oxygen and nitrogen contents may not be significant since the argon atmosphere in the syringe puller contained variable amounts of oxygen and probably also nitrogen.

TABLE VI

Element	Distribution coefficients found This work	In the literature
Pb	<0.7	<0.02
W	>1	
I	<0.3	
Sb	<1	
In	1,1, 0.1	
Zn	1,1, 1	1.9
Co	<1	≪0.02
Fe	0.3, 1,1, 0.5	0.3
Mn	<0.1	0.00004
Cr	<0.1, 0.3(a)	
Ca	2,2, 0.9	
K	1.5, 1,1	
Cl	<0.1, <0.1, <0.1	
S	1,1, <0.5	0.3
P	1	2
Si	0.1, <0.1	0.1
Al	>2.5, 1.2, 1,1	3
F	<1	
B	<0.1	
C	<0.1, 0.1	0.8
N	0.5	
O	0.3	

continued from previous column

(a) A direct determination of the distribution coefficient of chromium by comparing the concentration in the melt with that at the front of the crystal gives a value of 3 × 10^{-5}.

be correlated with electrical measurements, and the density of flat-bottomed etch pits can be correlated with the oxygen content.

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