JOURNAL OF MATERIALS SCIENCE 15 (1980) 2785–2794

# Impurities in single crystal indium phosphide

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The impurity concentrations in present low carrier concentration indium phosphide single crystals ($N_D - N_A = 2 \times 10^{15}$ to $5 \times 10^{15}\,cm^{-3}$) grown by the Czochralski technique have been measured by spark-source mass spectrometry and radio-gamma activation analysis and compared with both the polycrystalline source material and the excess indium produced during compounding and growth. The predominant impurities are shown to be carbon, oxygen and silicon but the segregation of lesser impurities into the excess indium has allowed some nineteen other elements which are likely to be present in indium phosphide to be identified. No consistent correlation is evident between the measured concentration of specific impurities and the ionized donor ($N_D$) and acceptor ($N_A$) impurity levels as determined from the free-electron concentration ($N_D - N_A$) and Hall mobility at 77 K using the Brooks–Herring theory.

## 1. Introduction

Data derived from electrical measurements, such as Hall mobility and carrier concentration, are useful means of assessing the electrically active impurity concentration of semiconducting materials such as indium phosphide (InP) but give no information about the chemical nature of the impurities and, apart from an assignation that the predominant impurities are acceptor or donor in character, do not differentiate between impurities. Undoped single crystals of InP grown by the liquid encapsulated Czochralski technique [1–3] are n-type and during the past decade the net carrier concentration has been steadily reduced from $10^{17}\,cm^{-3}$ to $10^{15}\,cm^{-3}$ with corresponding increases in mobility [1–8] so that material with carrier concentrations 77 K and mobilities in the ranges $2 \times 10^{15}$ to $5 \times 10^{15}\,cm^{-3}$ and 25 000 to $40\,000\,cm^2\,V^{-1}\,sec^{-1}$, respectively, can now be produced consistently. However, although chemical analysis of the impurities present in the higher carrier concentration material is available [2–4], little definitive information has been published about the source and levels of impurity in the current low ($N_D - N_A$) crystals. Similarly, few positive links have been forged for bulk materials between residual impurities and recent data available from photoluminescent and deep-level transient spectroscopic measurements [9–12].

In the present work, the chemical concentrations of impurities present in low free electron concentration single crystals of indium phosphide grown by the Czochralski liquid encapsulation technique have been determined by spark source mass spectrometry (SSMS) and radiochemical gamma photon activation analysis (RGAA). Comparison has been made between (a) single crystals and the polycrystalline material from which they were grown and (b) the use of silica and pyrolitic boron nitride (PBN) as the crucible material. Analysis of the residual indium present at the ends of both polycrystalline bars and single crystals has also been performed. Particular attention has been devoted to those elements which are an unavoidable feature of the growth environment at some stage such as C, O, Si, B and N but other impurities have also been quantified.

## 2. Experimental procedure

The specimens for analysis were cut from polycrystalline bars of InP, prepared by directional solidification of In-rich solutions at a phosphorus pressure of 7 atm by MCP Electronics Ltd, and from InP single crystals grown at RSRE by the liquid encapsulation technique from the polycrystalline bars [1] using automatic diameter control based on crucible weighing [13]. Specimens were also cut from the excess indium present in the horizontal boat after the polycrystalline InP had been crystallized. Both silica and boron nitride

0022–2461/80/112785–10\$03.00/0

TABLE I Carbon levels in InP: Single crystals

| Crystal number | L660* | L807 | L816 | L853* | L860 | L861 | L879 | L880 | L893 | L898† |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration (ppma) | 2.0 | 0.3 | 0.75 | 3.0 | 0.42 | 0.36 | 0.12 | 0.3 | 0.3 | 0.2 |

*PBN used as a melt container throughout.
†Double-pulled material.

containers were used in the polycrystalline preparation and in the single crystal growth. Heating is applied externally to the reaction vessel in the polycrystalline preparation but occurs within the growth chamber for single crystal growth by coupling radio-frequency power at 450 kHz directly to the carbon susceptor surrounding the crucible.

Analysis was carried out using spark source mass spectrometry (SSMS) and radiochemical gamma photon activation analysis (RGAA), as described previously by Blackmore *et al.* [14]. For a general survey of the impurity elements present, standard SSMS techniques were employed, but where low atomic number elements were determined, liquid helium cryogenic pumping was employed. RGAA was used particularly for analysis of the C and O concentrations.

## 3. Results and discussion

### 3.1. Carbon analysis

The carbon content of ten single crystals of InP, all nominally undoped n-type are listed in Table I. No marked differences are apparent in the analysis obtained by RGAA and SSMS and the mean value of 0.34 ppma ($\equiv 1.3 \times 10^{16}$ atoms cm$^{-3}$) which can be calculated for single-pulled material shows reasonable agreement with the range of values quoted earlier (0.06 to 0.3 ppma) for a comparable crystal, L374, using identical analytical techniques [14]. Significantly, material which has been double-pulled shows a slightly higher mean carbon concentration of 2.5 ppma (L660 and L853) which implies that carbon contamination during crystal growth is a possibility. The major carbon presence and possible source of contamination is the susceptor which is, nevertheless, physically separated from the melt by the silica crucible used to contain both the melt and the boric oxide encapsulant used to suppress decomposition.

TABLE II Carbon levels in InP: Source materials to single crystals

| In source material | InP polycrystalline bars | | | In excess from bar | Single crystal |
|---|---|---|---|---|---|
| | Front | Middle | Rear | | |
| 4.8 | 0.2 | NA | NA | 5.7 | 0.3 (L807) |
| 1.9 | 0.5 | 1.8 | 1.2 | 8.6 | 0.42 (L860) |
| 5.7 | 0.4 | 0.3 | 0.6 | 3.8 | 0.36 (L861) |
| NA | 0.1 | NA | 1.7 | NA | 0.12 (L879) |
| NA | 0.3 | NA | NA | 4.5 | 0.2* (L898) |

*PBN used as a melt container throughout.
NA = Not analysed.

The amount of carbon in the polycrystalline bars of InP, used as starting material for Czochralski growth, shows interesting segregation effects with respect to both the source In and the In excess from the InP compounding process. Table II clearly shows that carbon segregates preferentially into the In excess but that only minor variations occur along the InP bars. However, the consistent equivalence between the values for the front end of the bar and the single crystal suggest that the general trend to a higher carbon content at the rear end of the polycrystalline bars is a real effect.

The segregation of carbon into the excess In continues through the single crystal growth, as shown in Table III, where the small amount of In remaining in the crucible after growth is found to have an enhanced carbon content with respect to the single crystal. Insufficient data are available to determine accurately any variations in carbon content produced along the crystal length by segregation effects but the existence of such changes must clearly be recognized on the basis of the present work.

TABLE III Carbon levels in InP: Complete single crystal analysis

| InP polycrystalline charge | | Single crystal | | In excess from single crystal | |
|---|---|---|---|---|---|
| Front | Rear | Top | Bottom | | |
| 0.1 | 1.7 | 0.1 | 0.1 | 0.7 | (L879) |
| 0.2 | 0.3 | 0.3 | 0.6 | 3.0 | (L880) |

The carbon level in the excess indium is not inconsistent with the amount present in the

TABLE IV Oxygen levels in InP: Single crystals

| Crystal number | L660* | L807 | L816 | L853* | L879 | L880 | L893 | L898† |
|---|---|---|---|---|---|---|---|---|
| Concentration (ppma) | 0.6 | 0.2 | 0.3 | 1.2 | 2.3 | 0.9 | 0.3 | 0.2 |

*Double-pulled material.
†PBN used as melt container throughout.

source indium. However, the observed segregation plus the 20:1 reduction in the volume of In during the reaction

$$\text{In} + \text{P(reduction)} \rightarrow \text{InP} + \text{In(excess)} \qquad (1)$$

would be expected to lead to greatly enhanced carbon levels (> 40 ppm) in the In excess. As this does not occur some carbon must be lost during compounding but this also implies that no substantial pick-up of carbon occurs from the phosphorus. Corroborative evidence from phosphorus analysis is not available because of difficulties encountered in analysing this highly reactive element.

## 3.2. Oxygen analysis

The oxygen content of eight single crystals of InP, all nominally undoped n-type, are listed in Table IV. These show reasonable agreement between the two analytical techniques and allow a mean value of 0.75 ppma ($3 \times 10^{16}$ atoms cm$^{-3}$) to be calculated. This is somewhat higher than the range of 0.05 to 0.3 ppma quoted for crystal L374 in earlier work but the present work covers many more samples. No significant difference is discernible between single and double-pulled material nor between material prepared in silica or PBN.

A comparison of Tables IV and V shows that the oxygen content of InP single crystals is lower than that of the In source material but evidence of segregation into the In excess must be considered inconclusive due to the possibility of contamination by either $SiO_2$ or $B_2O_3$. In the one case where such contamination was avoided, by the use of PBN container materials (see Table VI), only small changes were detected and although the oxygen level in the excess In is higher than in the polycrystalline bar and the single crystal, the changes are within experimental error.

## 3.3. Silicon analysis

The silicon contents of eight nominally undoped n-type crystals are listed in Table VII. These were all determined by SSMS and permit a mean level of 0.14 ppma ($6 \times 10^{15}$ atoms cm$^{-3}$) to be calculated for material which has been in contact with silica at some stage.

The information determined for the polycrystalline bars (Table VIII) is limited but shows consistency from bar to bar. There is evidence that silicon is rejected into the excess In for material prepared either in silica or PBN boats. The pick-up of silicon from silica crucibles during crystal growth is suggested by a comparison of crystals L893 and L898. Both were grown from the same polycrystalline material prepared in a PBN boat. This was converted into single crystal (L893) using a silica crucible to contain the melt and an increase in silicon content from 0.06 ppma in the polycrystalline bar to 0.3 ppma in the single crystal was observed. When identical polycrystalline material was converted into single crystal L898, using a PBN crucible to contain the melt, the silicon content remained relatively unchanged at 0.07 ppma.

TABLE V Oxygen levels in InP: Source materials to single crystals

| In source material | InP polycrystalline bars | | Single crystal | | In excess from single crystal |
|---|---|---|---|---|---|
| | Front | Rear | Top | Bottom | |
| 6.5* | 0.7 | 1.4 | 2.3 | 0.9 | 35 000† (L879) |
| 8.7 | 68.2 | 5.4 | 0.9 | 14.6 | 73 (L880) |
| 8.7 | | | | | |
| 24.4 | | | | | |

*Typical results for In source material but not material used directly for the bars in this table.
†High value due to entrapped $B_2O_3$.

TABLE VI Comparison of impurity levels detected in polycrystalline bars of InP, excees In from the bars, single crystal InP and excess In from the crystal

| Element | Polycrystalline InP | Excess In | Single crystal InP | Excess In |
|---|---|---|---|---|
| B | 0.01 | 0.2 | < 0.01 | 0.25 |
| C | 0.3 | 4.5 | 0.3 | ⩽ 3 |
| N | 0.06 | 0.1 | 0.03 | ⩽ 0.2 |
| O | 0.3 | 0.45 | 0.2 | ⩽ 1.2 |
| Al | 0.01 | 0.2 | < 0.03 | 0.15 |
| Si | 0.06 | 0.45 | 0.07 | 0.2 |
| Cl | 0.01 | ⩽ 1 | ⩽ 0.2 | ⩽ 1.5 |
| K | < 0.01 | 0.09 | < 0.01 | 0.02 |
| Ca | 0.02 | 0.3 | 0.03 | 0.1 |
| Cr | < 0.01 | < 0.03 | 0.01 | 0.15 |
| Fe | < 0.01 | 0.1 | 0.01 | 0.65 |
| Ni | < 0.03 | 0.15 | < 0.01 | 0.08 |
| Cu | 0.08 | 2.5 | < 0.02 | 1.0 |
| Zn | < 0.02 | 0.2 | < 0.01 | 0.02 |
| Ga | 0.05 | < 0.05 | 0.05 | 0.05 |
| As | < 0.01 | 0.04 | < 0.01 | 0.15 |
| Tl | < 0.01 | < 0.04 | < 0.01 | 0.04 |
| Pb | < 0.01 | 0.2 | < 0.02 | 0.01 |
| Bi | < 0.01 | 0.2 | < 0.01 | 0.03 |

All materials prepared in PBN containers.

## 3.4. Nitrogen and boron analysis

The concentration of nitrogen in single crystals of undoped InP is low throughout and shows no significant change between single- and double-pulled material nor between the use of silica or PBN container materials. A mean value of 0.05 ppma ($2 \times 10^{15}$ atoms $\text{cm}^{-3}$) can be calculated from the data presented in Table IX A and B.

A similar situation occurs for boron where a mean value of 0.07 ppma ($3 \times 10^{15}$ atoms $\text{cm}^{-3}$) can be calculated. However, this value is excessively weighted by the unexplained high value of L853; the mean of the other five determinations is 0.01 ppma ($4 \times 10^{14}$ atoms $\text{cm}^{-3}$).

## 3.5. Analysis for other elements

The SSMS analysis of InP single crystals for elements other than those described above is summarized in Tables X and XI. Thirteen elements, Na, Mg, Al, S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn and Ga have been detected at levels of 0.01 ppma ($4 \times 10^{14}$ atoms $\text{cm}^{-3}$) or greater, but none show a consistent presence throughout the series of eight crystals examined. Of the elements present, Cu in L660 (0.2 ppma) and L853 (0.3 ppma), S in L816 (0.2 ppma) and Na in L898 (0.7 ppma) represent the highest values. Fe (0.01 to 0.06 ppma) is present in five of the samples whilst Zn (0.04 to 0.15 ppma), Na (0.03 to 0.7 ppma), Ca (0.01 to 0.03 ppma), K (0.01 ppma) and Cl (0.01 to 0.2 ppma) are present on four occasions.

No consistent pattern emerges from this data about which elements, in addition to the light elements delineated in Table IX, are likely to be present in all cases and particularly about which elements occur at concentration levels below 0.03 ppma ($\sim 10^{15}$ atoms $\text{cm}^{-3}$) and could impair or modify the electrical characteristics of the material.

A much clearer pattern of the elements likely to be present can be obtained by using the preferential segregation of impurities from InP into the excess In, which was first observed for carbon (see Section 3.1) but also occurs for other elements, as shown in Table VI. This preferential segregation concentrates impurities to levels where

TABLE VII Silicon levels in InP: Single crystals.

| Crystal number | L660* | L807 | L816 | L853* | L860 | L861 | L893 | L898† |
|---|---|---|---|---|---|---|---|---|
| Concentration (ppma) | 0.15 | 0.15 | 0.1 | 0.35 | 0.01 | 0.01 | 0.3 | 0.07 |

*Double-pulled material.

†PBN used as melt container throughout.

TABLE VIII Silicon levels in InP: Source materials to single crystals

| In source material | InP polycrystalline bars | | | In excess from bars | Single crystal |
|---|---|---|---|---|---|
| | Front | Middle | Rear | | |
| 0.06 | 0.3 | 0.6 | 1.5 | NA | 0.01 (L860) |
| 0.2 | 0.08 | 0.06 | 0.04 | 0.3 | 0.01 (L861) |
| NA | NA | 0.06 | NA | 0.45 | 0.3* (L893)<br>0.07† (L898) |

NA = Not analysed.

*Polycrystalline bar prepared in PBN, single crystal prepared in silica.

†PBN used as melt container throughout.

they can be measured realistically. Hence, it is obvious from Table VI that, in addition to the light elements (B, C, N, O and Si) already discussed, the presence of Al, Cl, K, Ca, Cr, Fe, Ni, Cu, Zn, As, Tl, Pb and Bi can be confirmed. The apparent absence of these elements in the single crystal InP merely suggests that they occur at levels below 0.01 ppma (i.e. below $4 \times 10^{14}$ atoms $\text{cm}^{-3}$). This argument takes no account of impurities which might segregate preferentially into the InP but as the analysis of both single crystal and polycrystalline material shows no impurity enhancement, it may be concluded that no significant impurity behaves in this way.

## 3.6. Impurity levels and electrical characteristics

The room temperature and liquid nitrogen temperature Hall mobilities and the liquid nitrogen temperature carrier concentrations ($N_D - N_A$) are summarized for the ten crystals used during this work in Table XII. No significant differences were observed in the measurements along the crystal length so that only the values obtained at the seed-end of the crystals are quoted.

The analytical data for impurities present is also summarized in Table XII. From this data, the ionized donor ($N_D$) and acceptor ($N_A$) impurity levels and, hence, the total ionized impurity content ($N_D + N_A$) have been calculated using the measurements of free electron concentration ($N_D - N_A$) and Hall mobility at 77 K and the Brooks–Herring theory [15] in the manner described by Mullin *et al.* [3]. As in their work, it was assumed that any deep donors would be neutral at 77 K and would play an insignificant role in such an analysis. Values of the effective electron mass ($m^*$) = 0.08 and the dielectric constant ($\epsilon$) = 12.5 and a lattice mobility of 400 000 $\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$ were used in these calculations. The ionized impurity and lattice mobilities were combined by reciprocal addition. The calculated values of $N_D$ and $N_A$ and the concentrations of the major impurities are compared in Table XIII. It is clear from this table that carbon, which is suggested to be a shallow acceptor [9], does not equate with $N_A$ and that oxygen, whose role is not clear but is likely to be a deep-level donor and therefore unlikely to be ionized at 77 K, does not equate with $N_D$. Hence, there is no direct correlation between $N_D$, $N_A$ and the two major residual impurities. The situation for the next most prevalent impurity, silicon, is less clearly defined. Crystals L660, L807, L816 and L853 show reasonable agreement between $N_D$ and the chemical concentration of silicon as determined using an MS7 instrument, which is in agreement with the data published by Mullin *et al.* [3] using the same instrument but with slightly higher

TABLE IXA Nitrogen levels in InP single crystals

| Crystal Number | L660* | L807 | L816 | L853* | L893 | L898† |
|---|---|---|---|---|---|---|
| Concentration (ppma) | 0.07 | 0.06 | 0.04 | 0.07 | 0.07 | 0.03 |

*Double-pulled material.

†PBN used as melt container throughout.

ND = Not detected.

TABLE IXB Boron levels in InP single crystals

| Crystal number | L660* | L807 | L816 | L853* | L893 | L898† |
|---|---|---|---|---|---|---|
| Concentration (ppma) | 0.01 | ND | 0.04 | 0.4 | ND | ND |

*Double-pulled material.

†PBN used as melt container throughout..

ND = Not detected.

TABLE X Mean levels of light elements in InP single crystals

| Element | Concentration (ppma) |
|---|---|
| H | ND |
| Li | ND |
| Be | ND |
| B | 0.07 |
| C | 0.34 |
| N | 0.05 |
| O | 0.75 |
| F | ND |
| Na | ND to 0.07 |
| Mg | ND to 0.03 |
| Al | ND to 0.03 |
| Si | 0.14 |

ND = not detected.

silicon contents than those reported here. However, comparisons of L893 and L898 where the silicon content has been reduced by a factor of four show no ensueing significant change in $N_D$. Furthermore, analysis of L860 and L861, on a JEOL mass spectrometer, which has a potentially higher resolution for silicon, suggests that the silicon content could well be an order of magnitude lower at about 0.01 ppma. An analysis of a much earlier germanium-doped crystal (L757) using this latter instrument gave a silicon level of 0.03 ppma ($1.2 \times 10^{15}$ atoms $\mathrm{cm}^{-3}$) which is within a factor of three of the results for L860 and L861. Hence, any correlation of silicon content with $N_D$, at the low levels of carrier concentration now consistently produced, must be regarded as tenuous. However, Bass [16] has recently confirmed that silicon acts as a donor in InP produced by an alkyl process, so any silicon present will undoubtedly contribute towards $N_D$. The same work also suggests that material deliberately doped with oxygen becomes increasingly n-type. Hence, the possibility that a small amount of the oxygen detected in the bulk crystals contributes to $N_D$ cannot be ruled out.

The elements contributing to $N_A$ at this level are also hard to define. Zinc is a known acceptor but is not always present in detectable quantities and in only three cases (L816, L860, and L861) is there sufficient zinc present to account for $N_A$. In the remaining cases, contributions from other sources are required. A contribution from some of the carbon cannot be ruled out [9] and magnesium, when present, is a known acceptor, but the role of other likely acceptors such as sodium, potassium and calcium is unknown.

In the absence of a positive connection between values of $N_D$ or $N_A$ and specific impurities, further discussion tends to become speculative especially as the possible interaction of lattice vacancies is not understood at present. Nevertheless, it is interesting to note that the crystals with highest mobility (L816 and L807) have the lowest calculated $N_A$ value and that the crystal with the lowest mobility (L660) has the highest calculated $N_A$ value. Significantly both L816 and L660 contain substantial amounts of impurity compared to L893 which has only average mobility despite its high purity. Facts such as this undoubtedly add to the contention that lattice vacancies play some role in controlling the mobility in indium phosphide at low impurity levels. The coupling behaviour of $N_D$ and $N_A$ evident from Table XIII, whereby both values increase or decrease simultaneously, also lends support to such an argument.

### 3.7. Impurity sources

In view of the segregation of impurities into the excess In which occurs during the preparation of InP, high purity In is a prerequisite as a source material. Typical values for the impurity level in six samples of In are given in Table XIV. A comparison of Tables VI and XIV suggests that some

TABLE XI Other elements detected but not consistently present

| Crystal number | Element concentration (ppma) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | S | Cl | K | Ca | Cr | Mn | Fe | Cu | Zn | Ga |
| 660 | | | | 0.03 | | 0.01 | 0.04 | 0.2 | 0.04 | |
| 807 | | | 0.01 | | | | 0.01 | | | 0.2 |
| 816 | 0.2 | 0.2 | 0.01 | | | | 0.06 | 0.02 | 0.04 | |
| 853 | | 0.01 | | 0.01 | | 0.03 | 0.04 | 0.3 | | |
| 860 | | 0.1 | | | | | | | 0.15 | |
| 861 | | 0.02 | | 0.02 | | | | | 0.1 | |
| 893 | | | 0.01 | 0.03 | 0.01 | | 0.01 | | | 0.05 |
| 898 | | | 0.01 | | 0.01 | | | | | 0.06 |

TABLE XII Electrical measurements and impurity levels for InP single crystals

| Crystal number | Mobility ($cm^2 V^{-1} sec^{-1}$) | | Carrier concentration ($cm^{-3}$ at 77 K) | C (ppma) | O (ppma) | Si (ppma) | Others (0.01) |
|---|---|---|---|---|---|---|---|
| | at RT | at 77 K | | | | | |
| L660 | 4500 | 22 000 | $2 \times 10^{15}$ | 2 | 0.6 | 0.15 | B (0.01) N (0.07)<br>Na (0.07) Ca (0.03)<br>Fe (0.04) Mn (0.01)<br>Cu (0.2) Zn (0.04) |
| L807 | 5000 | 34000 | $3.9 \times 10^{15}$ | 0.3 | 0.2 | 0.15 | N (0.06) Na (0.03)<br>K (0.01) Ga (0.2)<br>As (0.02) |
| L816 | 5243 | 39407 | $3.4 \times 10^{15}$ | 0.75 | 0.3 | 0.1 | B (0.04) N (0.04)<br>Na (0.03) Mg (0.03)<br>Al (0.02) S (0.2)<br>Cl (0.2) K (0.01)<br>Fe (0.06) Cu (0.02)<br>Zn (0.04) |
| L853 | 3871 | 22801 | $5.4 \times 10^{15}$ | 3 | 1.2 | 0.35 | B (0.4) N (0.07)<br>Na (0.08) Al (0.03)<br>Cl (0.01) Ca (0.01)<br>Mn (0.03) Fe (0.04)<br>Cu (0.3) |
| L860 | 4830 | 25796 | $3.6 \times 10^{15}$ | 0.42 | NA | 0.01 | Mg (0.01) Cl (0.1)<br>Zn (0.15) |
| L861 | 4661 | 25870 | $3.3 \times 10^{15}$ | 0.36 | NA | 0.01 | Cl (0.02) Ca (0.02)<br>Zn (0.1) |
| L879 | 4598 | 29131 | $5.2 \times 10^{15}$ | 0.12 | 2.3 | NA | NA |
| L880 | 4587 | 30711 | $4.9 \times 10^{15}$ | 0.3 | 0.9 | NA | NA |
| L893 | 4636 | 27950 | $4.5 \times 10^{15}$ | 0.3 | 0.3 | 0.3 | N (0.07) Na (0.03)<br>Ca (0.03) Cr (0.01)<br>Fe (0.01) Ga (0.05) |
| L898 | 4807 | 26160 | $3.7 \times 10^{15}$ | 0.3 | 0.2 | 0.07 | N (0.03) Na* (0.75)<br>Cr (0.01) Ga (0.06) |

*Suspected contamination due to NaOH cleaning of crucible during manufacture.
NA = not analysed.

volatile impurities such as S and Hg are substantially removed during the compounding process, since they are not found in either the polycrystalline InP or the In excess. With the exception of the light elements, C and O, the level of the remaining non-volatile elements is substantially similar for both the In and polycrystalline InP and, hence, little contamination from phosphorus appears to occur apart from the incorporation of a small amount of arsenic, which

TABLE XIII Comparison of $N_D$, $N_A$ and major impurities of known donor/acceptor type

| Crystal number | $N_D$ (calc.) 77 K ($\times 10^{15}$ atoms $cm^{-3}$) | $N_A$ (calc.) 77 K ($\times 10^{15}$ atoms $cm^{-3}$) | Si (ppma) | C (ppma) | O (ppma) | Zn (ppma) |
|---|---|---|---|---|---|---|
| L660 | 6.3 | 4.3 | 6.0 | 80 | 24 | 1.6 |
| L807 | 5.8 | 1.9 | 6.0 | 12 | 8 | ND |
| L816 | 4.8 | 1.4 | 4.0 | 30 | 12 | 1.6 |
| L853 | 9.1 | 3.7 | 14.0 | 120 | 48 | ND |
| L860 | 5.9 | 2.3 | 0.4 | 17 | NA | 6 |
| L861 | 6.6 | 3.3 | 0.4 | 14 | NA | 4 |
| L879 | 7.8 | 2.6 | NA | 5 | 92 | ND |
| L880 | 7.0 | 2.1 | NA | 12 | 36 | ND |
| L893 | 7.1 | 2.6 | 12.0 | 12 | 12 | ND |
| L898 | 6.9 | 3.2 | 2.8 | 12 | 8 | ND |

NA = not analysed.
ND = not detected.

TABLE XIV Typical source In analyses (concentration values in ppma).

| Element | Sample Number | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| C* | 2.8 | 1.9 | 1.9 | 0.95 | 3.8 | 5.7 |
| O* | 6.4 | NA | NA | 8.7 | 8.6 | NA |
| Mg | 0.01 | 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| Al | 0.02 | 0.06 | 0.06 | 0.02 | 0.04 | 0.04 |
| Si | 0.04 | 0.06 | 0.2 | 0.02 | 0.03 | 0.2 |
| S | 0.05 | 0.06 | 0.06 | 0.01 | 0.05 | 0.3 |
| K | 0.05 | 0.02 | 0.06 | 0.01 | 0.05 | 0.01 |
| Ca | 0.04 | 0.08 | 0.08 | 0.01 | 0.03 | 0.04 |
| Ti | | 0.03 | | | | |
| Cr | | 0.02 | 0.03 | 0.01 | 0.04 | 0.03 |
| Mn | | < 0.01 | | | | |
| Fe | 0.01 | 0.03 | 0.01 | 0.07 | 0.04 | 0.03 |
| Ni | | < 0.01 | | < 0.01 | < 0.01 | 0.03 |
| Cu | 0.02 | 0.03 | 0.01 | 0.01 | 0.03 | 0.03 |
| Zn | | 0.01 | | | | |
| Hg | 0.01 | 0.07 | 0.01 | 0.03 | 0.01 | 0.01 |
| Tl | 0.1 | 0.03 | 0.15 | 0.04 | 0.1 | 0.03 |
| Pb | 0.04 | 0.08 | | | < 0.01 | 0.01 |
| Bi | 0.1 | 0.02 | | | | < 0.01 |

NA = Not analysed.
*Determined by RGAA.

is a well known impurity in phosphorus. Some purification is evident in the conversion to single crystal, a point which is substantiated by the lower levels of impurity found in excess indium from single crystal preparations compared with the levels found in the excess indium from polycrystalline preparations. This gradual improvement in purity during the transition

$$\begin{aligned} \text{In} + \text{P} &\rightarrow \text{InP (polycrystalline)} \\ &\rightarrow \text{InP (single crystal)} \end{aligned} \qquad (2)$$

suggests that few additional impurities are added to the indium in compounding and single crystal growth. The exceptions appear to be the small amount of As, referred to above, and the possible contamination by C, O and Si from the containing boat or crucible and susceptor. Sn, which is usually a common impurity in In, has not been detected at all in this investigation.

The present work amply demonstrates the segregation of a substantial number of impurities into the excess indium, which forms principally

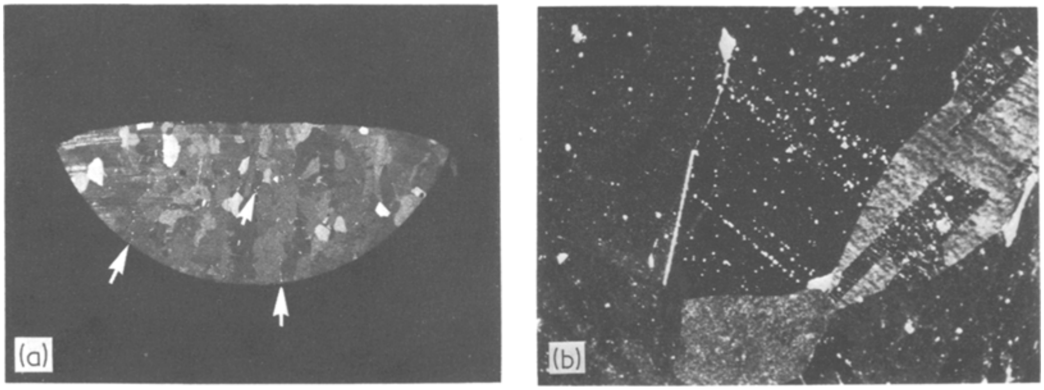

*Figure 1* Transverse sections from a horizontally-grown polycrystalline ingot of indium phosphide. (a) Showing typical indium metal entrapment at grain boundaries (marked by the arrowheads); the large bright areas are highly reflecting grains of indium phosphide (X 1.67). (b) Showing indium metal (the white areas) entrapped both at grain boundaries and within the grains (X 22.3).

during the compounding of In and P to form polycrystalline InP, and also to a lesser extent during single crystal growth. During polycrystalline growth, indium can be trapped easily at grain boundaries and within the grains as shown in Fig. 1. Such entrapped material must also contain segregated impurities and, upon remelting, these impurities must inevitably disperse and become a source of contamination during subsequent crystal growth from such material.

Under these circumstances, the level of impurities in single crystals is controlled by further rejection of impurities into the residual indium segregated during growth and a competing process which is the possibility of further contamination, however small, from the growth environment. Hence, the use of pure indium and the removal of all excess indium during polycrystalline preparation are essential conditions in order to obtain the purest material; the high values of mobility ($91\,000\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}$) and low value of carrier concentration ($6.9 \times 10^{14}\,\mathrm{cm}^{-3}$) obtained by Antypas [7] on a single grain extracted from a polycrystalline bar lend strong support to this argument. Nevertheless, the presence of excess indium during polycrystalline preparation does appear to be beneficial provided it can be separated efficiently from the InP. Another important point which emerges from this analysis is that the production of InP using high pressure processes without excess indium would lead inevitably to the entrapment of the non-volatile impurities which normally segregate into the excess.

## 4. Conclusions

SSMS and RGAA analysis of indium phosphide crystals grown by the Czochralski technique have shown that the major impurities present in low carrier concentration material ($N_\mathrm{D} - N_\mathrm{A} = 2 \times 10^{15}$ to $5 \times 10^{15}\,\mathrm{cm}^{-3}$) are carbon (mean level of $1.3 \times 10^{16}$ atoms $\mathrm{cm}^{-3}$), oxygen (mean level of $3 \times 10^{16}$ atoms $\mathrm{cm}^{-3}$) and silicon ($6 \times 10^{15}$ atoms $\mathrm{cm}^{-3}$), although the latter figure appears to be sensitive to the particular instrument employed and must be regarded as an upper limit. Boron and nitrogen are present at mean levels of approximately $2 \times 10^{15}$ atoms $\mathrm{cm}^{-3}$.

The segregation of impurities into the excess indium produced during both polycrystalline and single crystal preparation shows that up to 17 other elements can be present at levels which are generally lower than $1 \times 10^{15}$ atoms $\mathrm{cm}^{-3}$ but which can be occasionally higher. These are: Na, Mg, Al, S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn, Ga, As, Tl, Pb and Bi.

Some evidence exists to suggest that the silicon content of InP can be reduced by the use of pyrolitic boron nitride as a container material and the use of excess indium in the preparative procedure is shown to be beneficial.

No consistent correlation is evident between specific impurity concentrations and values of $N_\mathrm{D}$ and $N_\mathrm{A}$ calculated from the measured Hall mobility and free-electron concentration at 77 K.

## Acknowledgements

The authors wish to acknowledge the help of the following: G. W. Blackmore and C. Dowding (AMTE, Holton Heath) for providing most of the SSMS data, Plessey Research (Caswell) for providing the remainder of the SSMS data, ARDU (AERE, Harwell) for the RGAA data, Dr J. Wardill and S. F. Lovett (MCP Electronics Ltd, Foliejon Park, Windsor) for the provision of polycrystalline InP and In samples, Dr S. J. Bass (RSRE, Baldock) for permission to quote his unpublished work, and our colleagues Dr J. B. Mullin and Miss A. M. Royle for very helpful discussions. This article is published with permission of the Ministry of Defence who retain copyright of the article.

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Received 28 February and accepted 31 March 1980.