# Vapour phase preparation of indium phosphide in large quantities

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Several chemical reactions are investigated with the objective of producing indium phoshide in a form suitable for single crystal growth. The most suitable reaction for this purpose and the nature and quality of the product are described.

## 1. Introduction

The compound indium phosphide is being studied as a potential semiconductor device material and a considerable effort has been expended to provide first, a source of material for single crystal growth, second to produce single crystals and third to produce epitaxial layers. At present, material for stage one is prepared by direct reaction between indium metal and phosphorus, in silica glass tubes at a temperature of about 1000° C, under phosphorus pressures of several atmospheres. An improved process would be one where a lower temperature and pressure were used and where the introduction of impurities into the product was reduced. This work describes experiments with alternative methods for production of source material with the above objectives being criteria for process selection. Some of the methods investigated were those first investigated by Effer [1]. These workers investigated the reactions between indium monochloride and phosphorus or phosphine and between phosphorus trichloride and indium metal. They concluded that the last reaction was probably the best for the production of indium phosphide principally on the grounds that the trichloride could be raised to a high degree of purity. The work below records the results of a further study of these reactions, other additional reactions and the preparation of bulk indium phosphide using the reactions.

## 2. Experimental

The reagents used were high purity indium monochloride, indium trichloride phosphorus, phosphorus trichloride, phosphine and hydrogen gas. The maximum total impurity content of any of these reagents was 50 ppm. The former four reagents were supplied in sealed glass ampoules, the latter two reagents were obtained from the manufacturers in cylinders. The first apparatus used was a two zone horizontal furnace and the solid reagent was placed in a silica glass boat inside a silica glass tube which passed through this furnace with entry and exit connections for the required gases at each end of the tube. A second apparatus is shown in Fig. 1 designed as a result of experiments using the first apparatus. This equipment has the single zone furnace mounted vertically controlled by an electronic controller to ± 1° C. The glass used is silica glass. The relevant gases are brought to the equipment through PTFE pipes of 4 mm bore. An identical furnace unit is placed in series with the first to eliminate any impurities due to back diffusion from the exit before they reach the first reaction vessel. This trapping reactor is loaded with the same reactants as the first reactor and in addition to the main function also uses any excess of reactant gas reaching it from the first reactor. The outer tube of the reaction chamber is 30 cm long and 30 mm diameter and the inner tube is 20 cm long and 20 mm diameter. They are connected as shown by a PTFE joint. Indium monochloride as received from the manufacturers is a pale yellow solid which melts at 225° C to give a red liquid, and which boils at 508° C. On cooling this rapidly can give an orange-red solid. The solid is hygroscopic and the loading from capsule to reaction tube is made in a dry box flushed with dry nitrogen. Indium trichloride is a white solid which has a high vapour pressure and commences
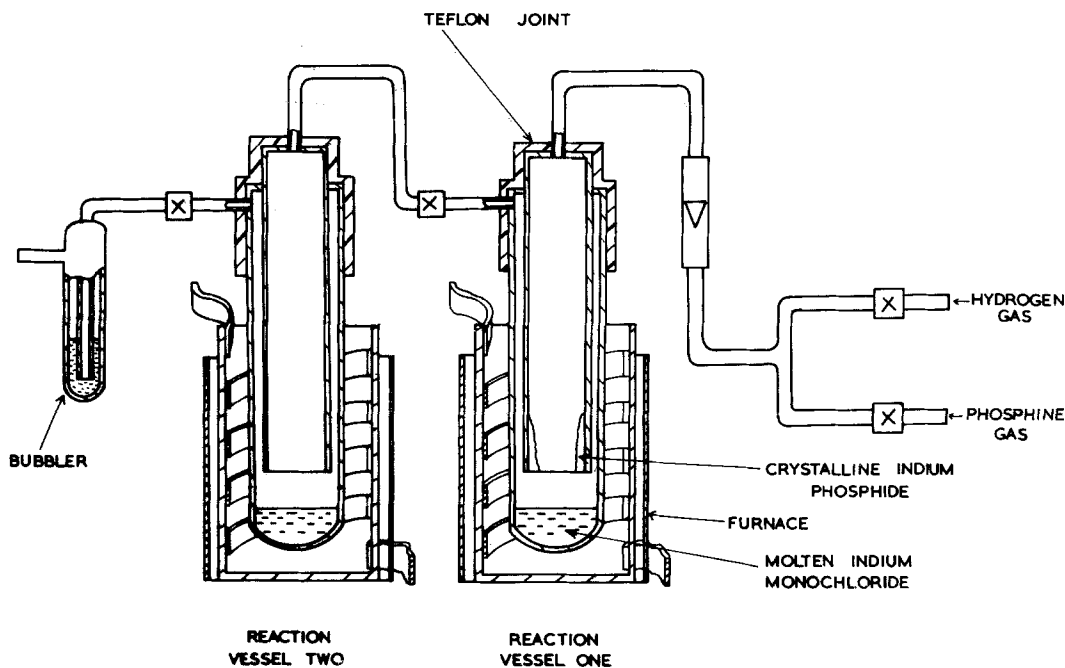
*Figure 1* The arrangement of the apparatus used to produce indium phosphide from the reaction of indium monochloride and phosphine.

to sublime to a considerable extent at about 300° C, melts at 586° C and is completely volatile at 600° C. It is much more hygroscopic than the monochloride and is consequently more difficult to manipulate and maintain free of water. Indium monobromide is an orange-red solid melting at 220° C and subliming at 600° C. It is less hygroscopic than the chlorides.

## 3. Results

The previous workers tested the following reactions for the production of indium phosphide, first indium monochloride and phosphorus, second indium monochloride and phosphine and third indium metal and phosphorus trichloride.

They found that the reactions were complex and the exact nature of the reaction products was not easy to define. There are other reactions which are possible but it was not known whether indium phosphide was produced and whether or not it was efficiently produced. These reactions were hence investigated, and they are first indium trichloride and phosphine, second indium monochloride, phosphorus trichloride and hydrogen, and third indium monobromide and phosphine.

Of the former group of reactions the third is used to produce epitaxial layers of indium phosphide [2]. Experiments showed that as a production process it is a relatively slow reaction but more

important it gives rise to a considerable amount of by-products, particularly phosphorus, making it unsuitable for the present objective.

The reaction with the vapour of indium monochloride and phosphorus at temperatures in the range 200 to 500° C does proceed slowly giving indium phosphide, but the rate is too low to make it suitable for the production of material for crystal growth.

The reaction between indium monochloride and phosphine gave the following results. In this reaction the phosphine/hydrogen mixture was first passed over the molten monochloride in a silica glass boat. Under these conditions the peculiar behaviour of molten monochloride was first observed At a temperature of about 300° C the monochloride tends to rise up over the walls of the boat and flow out. Moreover the reaction which produced indium phosphide at temperatures of between 300 and 600° C was observed to take place not between the liquid monochloride and phosphine but between the vapourized indium monochloride and phosphine. Even under these conditions, however, the reaction appeared to be very efficient in producing indium phosphide. The system in Fig. 1 was then made to overcome the containment problem and to collect the indium phosphide formed in the vapour phase. In this system the indium monochloride is maintained at

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TABLE I

| Experiment code | Temperature | | Wt InCl used (g) | Wt InP formed (g) | Efficiency (%) | Conversion time and nature of InP |
| --- | --- | --- | --- | --- | --- | --- |
| | InCl | Collector | | | | |
| GC 17 | 600 | 430 | 25 | 19.2 | 79.2 | 30 h, compact polycrystalline mass |
| GC 19 | 600 | 430 | 25 | 18.1 | 74.6 | 29 h, compact polycrystalline mass |
| GC 20 | 600 | 430 | 25 | 14.5 | 59.8 | 20 h, compact polycrystalline mass |
| GC 21 | 600 | 430 | 25 | 12.5 | 51.6 | 30 h, compact polycrystalline mass |
| GC22 | 600 | 430 | 25 | 14.4 | 59.8 | 30 h, compact mass Some needles |
| GC 23 | 700 | 600 | 25 | 15.7 | 64.7 | 28 h, as above |
| GC 36 | 650 | 612−537 | 25 | 19.0 | 78.3 | 27 h, as above |
| GC 37 | 650 | 612−537 | 25 | 18.0 | 74.2 | 28 h, as above |
| GC 38 | 650 | 612−537 | 25 | 25.0 | Approaching 100 | 30 h, as above Excess monochloride and phosphorus present |
| GC 39 | 650 | 612−537 | 25 | 18.0 | 74.2 | 28 h, as above |
| GC 40 | 650 | 612−537 | 25 | 17.7 | 73.0 | 32 h, as above |
| GC 41 | 650 | 612−537 | 25 | 21.3 | 87.8 | 24 h, as above |
| GC 42 | 650 | 612−537 | 25 | 18.3 | 75.5 | 22 h, as above |
| GC 43 | 650 | 612−537 | 25 | 18.3 | 75.5 | 24 h, as above |

or slightly above its boiling point in the base of the outer test tube and the vapour from it made to react with the phosphine inside the collector tube. Any unreacted indium monochloride condenses and returns to the base of the inner tube. These conditions were achieved by using a furnace with a temperature profile which held the indium monochloride at a temperature of 600° C and the reaction zone at 600° C maximum and 375° C minimum. The phosphine/hydrogen gas mixture had a flow rate of $50 \, cm^3 \, min^{-1}$ for the most efficient production and the phosphine concentration in the gas stream was 5%. The reaction system described is a reflux system and hence tends to separate any non-volatile impurities from the monochloride and any volatile impurities which condense at a lower temperature than indium monochloride. On completion of the reaction the collector tube is removed and the indium phosphide extracted. The reaction is efficient and Table I lists details of several preparations The majority of the indium phosphide forms on the inside of the coll-



*Figure 2* Samples of compact indium phosphide prepared by the reaction of indium monochloride and phosphine.

ector tube as a hard compact microcrystalline mass as shown in Fig. 2 in a temperature zone of 475° C minimum and 575° C maximum, the thickest part of the deposit being at a temperature of 525° C. No other solid products were observed to be formed during the reaction with the exception of a little phosphorus. Since the latter could arise from the thermal decomposition of the excess phosphine the reaction can be written:

$$InCl + PH_3 \rightarrow InP + HCl + H_2.$$

A similar equation is possible if indium monochoride is considered dimorphic in the vapour phase.

Indium phosphide is produced in the reaction between indium monochloride, phosphorus trichloride and hydrogen, and between indium monobromide and phosphine, using the equipment shown in Fig. 1, with conditions of temperature and gas flow rate very similar to those for the above reaction. However, the amount produced in each case is very much less than is the case with the monochloride. The same is true of the reaction between indium trichloride and phosphine.

Hence the reaction of indium monochloride and phosphine is the most efficient for the production of indium phosphide in quantity. Several hundred grams of the compound were produced and used successfully to produce single crystals via the Czochralski process under pressure [3].

Crystal growth indicated that the material contains excess phosphorus, and possibly some

TABLE II

| Element | Concentration in InCl (ppm atomic) | Concentration in InP from InCl (ppm atomic) | Concentration in InP from InP (ppm atomic) |
|---|---|---|---|
| Bismuth | < 0.01 | 3.0 | < 0.01 |
| Lead | 0.6 | 0.1 | < 0.02 |
| Thallium | 0.3 | < 0.01 | < 0.01 |
| Mercury | < 0.03 | < 0.03 | 1.0 |
| Barium | 0.1 | 0.1 | < 0.03 |
| Iodine | < 0.1 | < 0.01 | < 0.01 |
| Cadmium | 0.04 | 1.0 | < 0.03 |
| Bromine | 20 | < 0.02 | < 0.02 |
| Arsenic | 3.0 | 0.3 | 0.3 |
| Gallium | 0.1 | < 0.02 | < 0.02 |
| Zinc | 0.1 | 3.0 | < 0.02 |
| Calcium | 3.0 | 10 | 0.1 |
| Potassium | 1.0 | 0.3 | 0.1 |
| Sulphur | < 1.0 | 1.0 | < 1.0 |
| Aluminium | 1.0 | 0.3 | < 0.03 |
| Sodium | 1.0 | 3.0 | < 0.3 |

indium monochloride. As a result the material tends to loose its compact nature and become slightly powdery on heating to melting temperature. However, excess phosphorus is not detrimental and the indium monochloride can be removed by vacuum heating at 300° C. The results of electrical measurements of some of the crystals showed them to have values of mobility at 300 K in the range 2500 to 3000 cm $V^{-1}$ $sec^{-1}$ and carrier concentrations at 300 K of $10^{16}$ to $10^{17}$ [4].

The results of mass spectrographic analysis of the monochloride and the phosphide produced from it are presented in Table II, along with an analysis of indium phosphide prepared by direct reaction of phosphorus and indium metal. These results indicate that, in general, the indium monochloride and the indium phosphide produced from it are less pure than indium phosphide at present available confirming the electrical results on grown crystals. In addition, since some impurities are not present in the chloride but do appear in the phosphide, this indicates that the phosphine is also a source of impurities.

## 4. Discussion

The results given have shown that the semiconducting compound indium phosphide can be produced in substantial quantities and in a compact form suitable for crystal growth using a vapour reaction. The results also show that from the reactions available the most suitable reaction is that between indium monochloride and phosphine. The reaction temperature is low, about 400° C lower than at present used, the pressure is atmospheric and the by-products minimal. In order to produce material of suitable purity, further purification of the indium monochloride and phosphine are required.

## References
1. D. EFFER and G. R. ANTELL *J. Electrochem. Soc.* 107 (1959) 252.
2. R. C. CLARKE, B. D. JOYCE and W. H. E. WILGOSS *Solid State Commun.* 8 (1970) 1125.
3. J. B. MULLIN, R. J. HERITAGE, C. H. HOLLIDAY and B. W. STRAUGHAN *J. Crystal Growth* 3, 4 (1968) 281.
4. P. TUFTON private communication (1974).