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The preparation of indium phosphide layers by chloride–hydride reactions

H. T. PARFITT, D. S. ROBERTSON
Royal Signals and Radar Establishment, Great Malvern, Worcestershire, UK

A. R. WILSON
BDH Chemicals Ltd, Poole, Dorset, UK

The preparation of indium phosphide by reactions between separate indium chlorides and phosphine is described. It is shown that the indium monochloride–phosphine reaction is the most favourable of the three possible reactions. It is demonstrated that various growth rates are possible over a range of temperatures, that good morphological layers can be obtained along with reasonable electrical characteristics. Explanations are advanced for the chemical process and the limitations on layer properties encountered.

1. Introduction

A study of the reaction between phosphorus trichloride, hydrogen and indium metal or solid indium phosphide has demonstrated that it is chemically inefficient [1]. An alternative reaction for layer production is the reaction between indium monochloride and phosphine which has been shown to be efficient [2]. The work below describes the results of a study of this reaction for use in the preparation of epitaxial layers of indium phosphide. In addition the reactions of other indium chlorides and phosphine were studied.

2. Experimental procedure

The equipment used is shown in Fig. 1, and consists of a horizontally mounted silica glass reaction tube, 150 cm long, and 3 cm diameter. This is enclosed for most of its length in a resistance wound furnance with three independently controllable heated zones. It is connected at one end to a source of hydrogen gas purified by palladium diffusion units. The other end consists of a system for unloading and loading necessary components into the reactor and a gas entry tube which has a silica glass support fitted to the end inside the reaction tube. Both ends of the reaction tube are enclosed in glove boxes continuously flushed with nitrogen purified by molecular sieve units to prevent entry to atmospheric gases, particularly water, into the reaction tube and to minimize any phosphorus fire hazard during loading and unloading operations.

A silica capsule of the solid indium chloride is placed at the left-hand end of the reactor tube. This is a "break-seal" capsule and the seal is only broken prior to loading into the reaction tube since the indium chlorides are hygroscopic. The single crystal slice of indium phosphide orientated on the selected orientation is polished to a featureless finish by mechanical–chemical means using 4% bromine–methanol on a fibre pad. After demounting the degreasing it is loaded on to the support tray at the end of the gas entry tube. The slice is then positioned in the appropriate zone. A gas mixture of phosphine in hydrogen enters the reaction tube via this latter gas inlet. All gases exit at a point at the right-hand end of the reactor. The system is operated by first raising the empty zone and the zone containing the substrate to operating temperature with the phosphine–hydrogen flowing. This required 7 min. Heating of the indium chloride capsule is then commenced after 4 min. When the capsule has reached operating temperature, growth is timed from this point and the growth period was normally 1 h. On completion of the growth period all heating systems were switched off simultaneously and the phosphine flow maintained till the system cooled to room temperature.

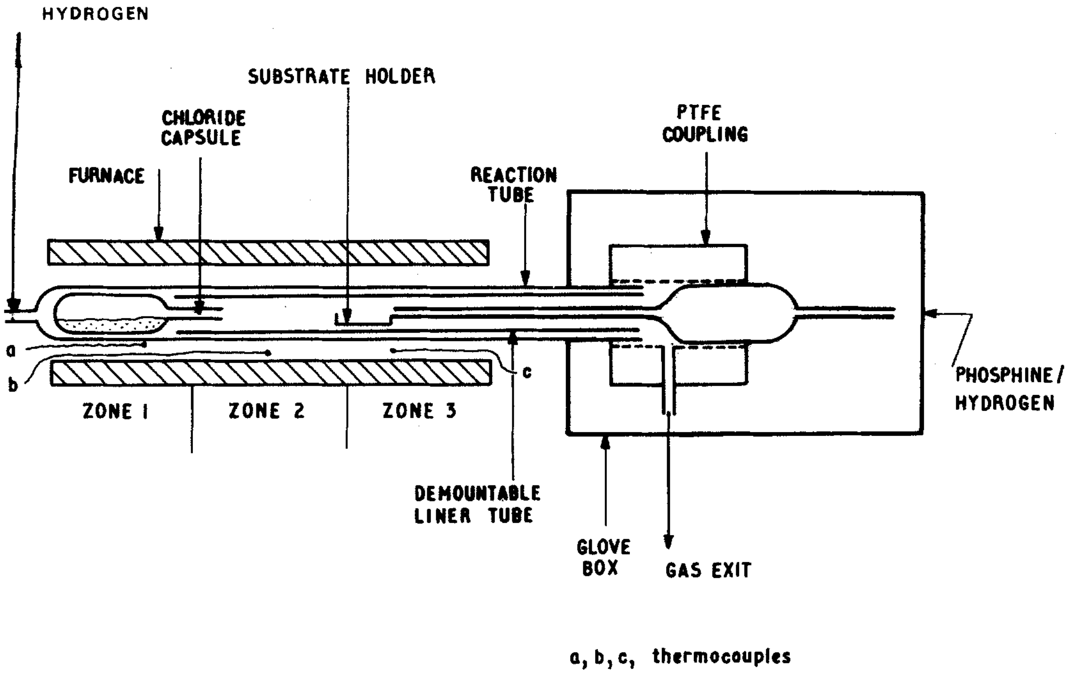

Figure 1 The reactor system used.

Various orientations of substrates were investigated and the layer thickness was monitored by cleaning and staining using the technique of Joel [3]. The electrical characteristics were monitored by means of the Van de Pauw technique using clover leaf specimens abrasively machined from the samples.

3. Results

The chlorides of indium have been subjected to extensive study. The existence of three chlorides of indium have been claimed. These are indium monochloride ($InCl$), indium dichloride ($InCl_2$) and indium trichloride ($InCl_3$). All of these halides were prepared for this work.

Indium trichloride was prepared by the direct reaction of chlorine and indium metal at 520° C. The monochloride was prepared first by the reduction of the trichloride with indium metal and second by the direct reaction of hydrogen chloride gas with indium metal. Both these reactions took place at 350° C. The formed monochloride was purified by vacuum distillation or zone refining, before being sealed into the capsules described, in a dry nitrogen atmosphere. It was found, however, that the product of the reaction of indium metal with hydrogen chloride was dependent on the degree of excess of the latter used during the reaction. If virtually no excess was used the product analysed as indium dichloride, whereas a large excess produced monochloride. Indium trichloride as prepared was white in colour, monochloride a pale green colour and dichloride white.

The reactions of each of these halides with phosphine were not the same. In the system described it is possible to perform the required reaction in two ways. In each of these modes of operation, the amount of chloride in the gas stream is controlled by the chloride capsule temperature. The range of heating is between the melting point and boiling point of the chloride involved. Experiment showed that for all the halides this range of temperature lay between 250 and 630° C. The volatilized chloride is carried towards the seed in the heated zone by the hydrogen flow. Operating the system as a two zone furnance, the left-hand zone (zone 1) containing the halide capsule and the second zone (zone 2) heated to the operating temperature (zone 3 being unheated) gave the following results. Indium trichloride produced virtually no indium phosphide irrespective of the capsule temperature, the phosphine concentration or the seed zone temperature. Indium dichloride produced indium phosphide with a reaction zone temperature as low as 350° C. Layers were of reasonable morphology, with a growth rate up to 5 $\mu m\ h^{-1}$ and the electrical characteristics as given in Table I.

TABLE I

Layer code	Halide	Temperature (° C)			Gas flows (ml mm^{-1})			Layer thickness (μm)	Electrical characteristics			
		Zone 1	Zone 2	Zone 3	Hydrogen over halide	Hydrogen with phosphine	Phosphine (concentration)		300 K		77 K	
									$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})
PV228A	$InCl_2$	575	650	650	100	90	10(100%)	No layer				
PV229A	$InCl_2$	625	650	650	100	90	10(100%)	No layer				
PV230A	$InCl_2$	625	450	450	100	90	10(100%)	8	Surface poor			
PV232A	$InCl_2$	500	500	500	100	90	10(100%)	7	1.3×10^{17}	237	1.9×10^{16}	403 p-type
PV233A	$InCl_2$	500	500	500	100	90	10(100%)	8	4.5×10^{16}	81	3.3×10^{15}	186 p-type
PV234A	$InCl_2$	500	450	450	100	90	10(100%)	3	2.8×10^{18}	8	2.3×10^{17}	12 p-type
PV235A	$InCl_2$	500	450	450	100	90	10(100%)	4	2.2×10^{16}	2224	2.3×10^{16}	2082
PV198A	InCl	570	550	550	100	Nil	100(10%)	21	2.2×10^{16}	1024	1.2×10^{15}	11,594
PV199A	InCl	570	600	600	100	Nil	100(10%)	48–63	Surface poor			
PV200A	InCl	570	650	650	100	Nil	100(10%)	35	Surface poor			
PV201A	InCl	570	650	650	100	Nil	100(10%)	16–44	1×10^{18}	148	2.2×10^{19}	188 p-type
PV202A	InCl	570	650	650	100	Nil	100(10%)	58	3×10^{14}	2071	1.3×10^{13}	409
PV203A	InCl	570	700	700	100	Nil	100(10%)	39	1.8×10^{17}	86	1.2×10^{16}	340 p-type
PV204A	InCl	570	700	700	100	Nil	100(10%)	29–49	Surface poor			
PV205A	InCl	570	750	750	100	Nil	100(10%)	No layer				
PV206A	InCl	570	650	650	100	Nil	100(10%)	52	5.7×10^{14}	4119	2.4×10^{12}	12,345
PV207A	InCl	570	650	650	100	Nil	100(10%)	50	2.1×10^{13}	1939	6.7×10^{12}	10,579

The phosphine was supplied either as 100% or 10% in hydrogen.
Substrate orientation 2° off the 1 0 0 plane.

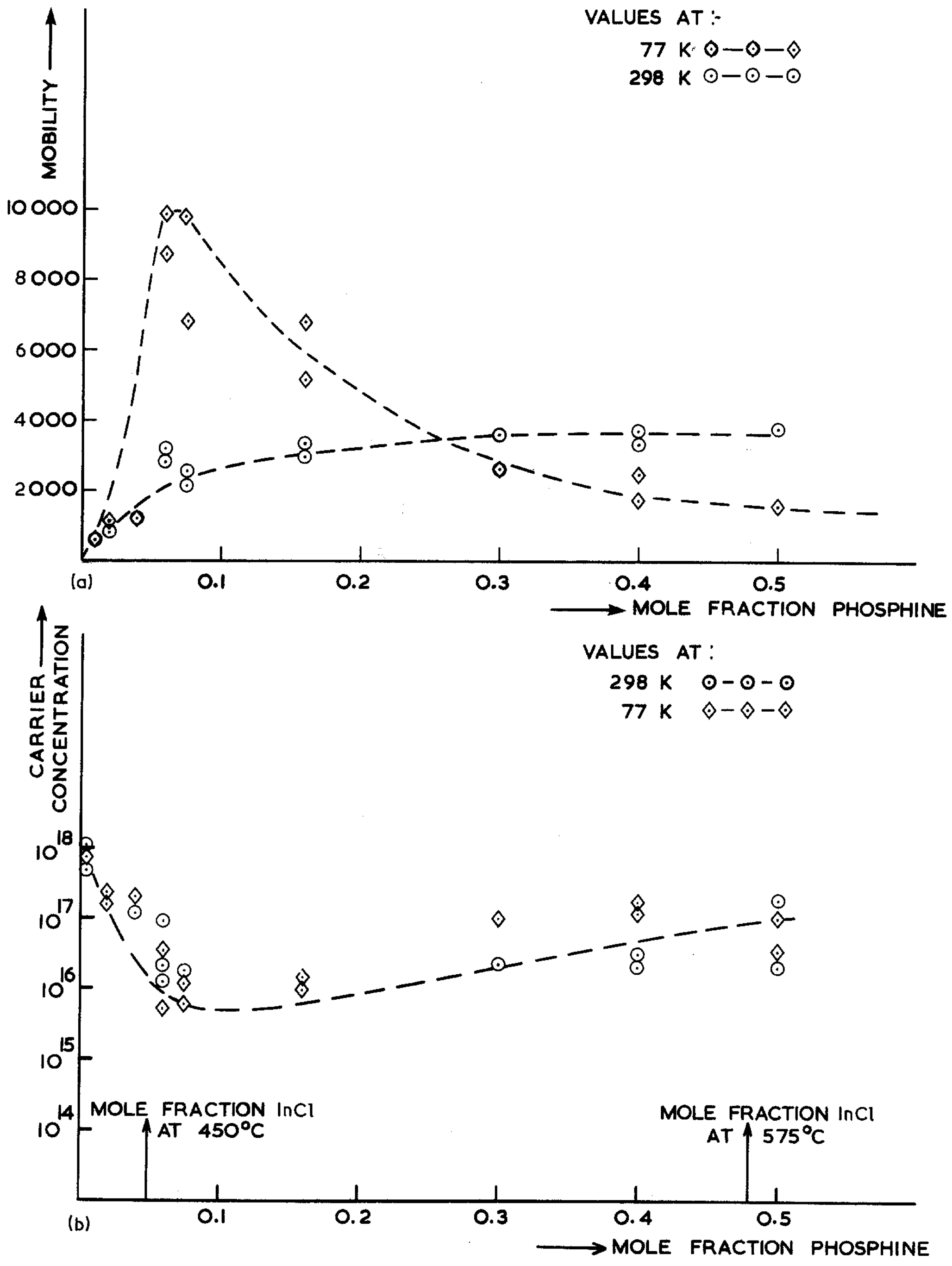

Figure 2 The variation of electrical characteristics of indium phosphide epitaxial layers produced at 450° C as a function of reagent concentration.

If the reaction zone temperature was increased the growth rate diminished and the indium phosphide deposited in cooler regions outside the furnace. The capsule temperature, phosphine concentration, gas flow rates or substrate orientation did not affect these results.

The indium monochloride produced vast amounts of indium phosphide under these operational conditions at a temperature of the seed zone of 450° C. However, the growth rate on the seed was limited to about 15 μm h^{-1} and was variable. The electrical characteristics varied as the phosphine concentration changed as shown in Fig. 2. In addition the morphology of the layers

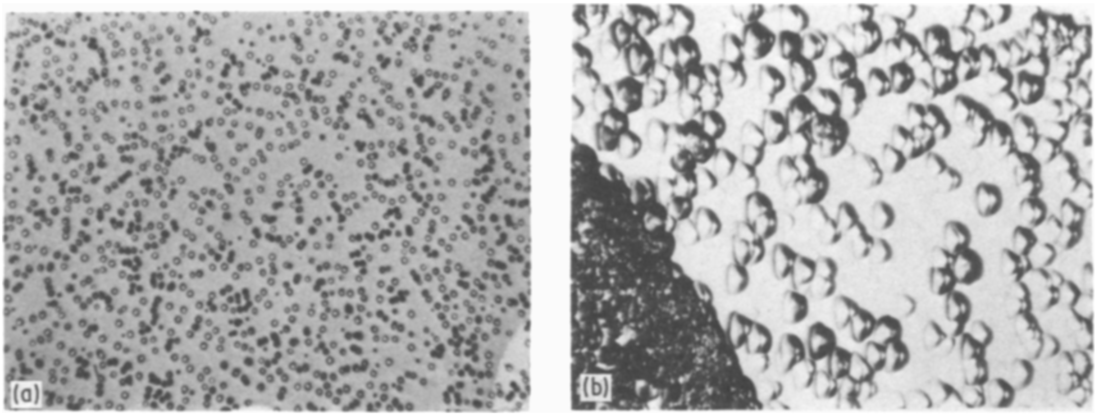

Figure 3 (a) Metallic globules on layer surface. (b) Hillocks on layer surface.

changed with reagent concentration. Using conditions which resulted in the monochloride being in excess, metal globules appeared on the surface. With phosphine in excess "hillock-like" features appeared. Both effects are shown in Fig. 3. As the seed zone temperature was raised the growth rate decreased and ultimately stopped, the indium phosphide depositing outside the furnance zone.

The second method of operating this system is, as before, with the chloride in zone 1 the seed in zone 2 and zone 3 is used to pre-heat the phosphine before reaction. Under these conditions the trichloride once again failed to produce any significant amount of indium phosphide. The dichloride produced layers up to 500° C pre-heat and growth temperature and thicknesses up to 10 μm. The monochloride produced layers up to 70 μm thick in 1 h at 650° C. A selection of the characteristics are given in Table I. In the case of the monochloride the amount of indium phosphide produced at high pre-heat and growth temperatures was markedly less than at low values of such parameters. Fig. 4 shows the change in growth rate at constant capsule temperature, as the growth and pre-heat temperature was progressively increased together. Fig. 5 shows the effect on growth rate of progressive increase in capsule temperature at constant pre-heat and growth temperature.

In the latter case the growth rate slowed down above 650° C and the layer morphology degenerated to the leaf-like structure shown in Fig. 6a.

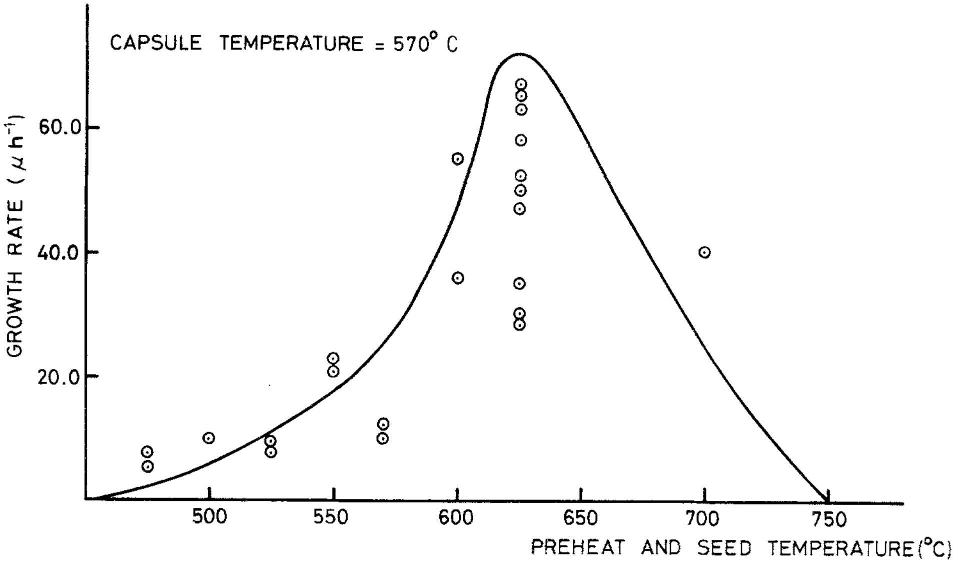

Figure 4 Growth rate as a function of preheat and growth temperature.

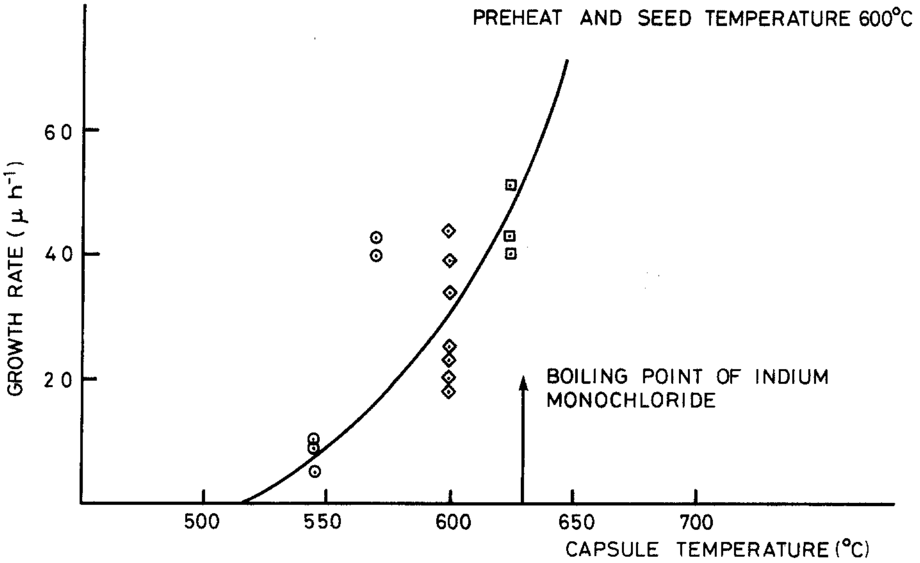

Figure 5 Growth rate as a function of the capsule temperature. The capsule holds in indium monochloride.

Under all of the above conditions changes in gas flow rates, substrate orientation or reagent concentration produced no very marked effects.

Under these conditions variability of growth rate was the rule. Table I also shows that variability of electrical characteristics was also the rule and that none of the layers obtained had properties in any way comparable to the best obtained by the trichloride-metal reaction previously studied [1]. In addition, p-type electrical characteristics were obtained most usually at the higher growth temperatures. Under both sets of operating conditions the monochloride reaction was efficient. About 30 layers could be produced from a 25 g capsule of monochloride. This is to be compared with 30 layers from 70 g metal in the trichloride metal systems. Finally layers could be obtained where the free electron concentration was apparently greater at low temperatures. These were associated with double layers as shown in Fig. 6b.

4. Discussion

The results show that the most favoured halide–hydride reaction for the production of indium phosphide epitaxial layers is that between indium monochloride and phosphine. This reaction can produce layers at reasonable growth rates with a

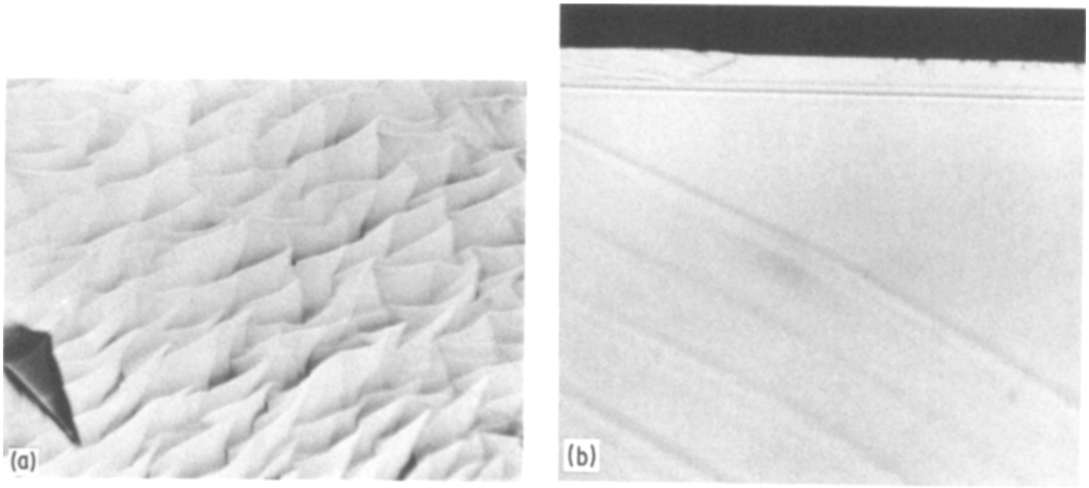

Figure 6 (a) Polycrystalline leaf structure obtained at 700° C preheat and growth temperature. (b) Double layers associated with inverted electrical characteristics.

range of substrate temperatures from 450 to 650° C. The morphological quality of the layers can be excellent. However, like the growth rate and electrical characteristics, this is variable.

In addition, the results show that the growth is related to the degree to which the phosphine is pre-heated. It can be concluded that high growth rates are a direct result of higher substrate temperature because the species forming the layer are more active at higher temperatures. However, this alone is not the entire explanation since high substrate temperatures without any pre-heating of the phosphine gave low or zero growth rates.

At temperatures up to 450° C it is clear that the reaction is between indium monochloride and phosphine. This is demonstrated by the large amount of indium phosphine produced under such conditions. In this instance the low substrate temperature clearly limited the growth rate. Above 450° C the progressive rise in growth rate was accompanied by a decrease in the amount of indium phosphide formed. The conclusion drawn from this is that not only was the substrate more active but that a different and more efficient set of layer forming species were formed by pre-heating the phosphine.

The previous work [1] concluded that phosphorus–hydrogen radicals resulting from the breakdown of phosphine formed initially were the basis of the reaction taking place near or on the substrate surface and resulting in layer formation. In this work no distinct evidence has been found to suggest that indium monochloride decomposes into radicals hence the higher growth rates must once again result from the breakdown of phosphine. This is certainly proceeding at 650° C. Thus phosphorus–hydrogen radicals are concluded to be involved. The fact that growth slows down at temperatures in excess of 650° C supports this in that a temperature must exist where the phosphine is completely decomposed into phosphorus species which do not react with indium monochloride. The results indicate this temperature to be 750° C.

Erstfeld and Quinlan [8] using a system closely related to that in the present work found that a temperature of the order of 900° C was required to produce the indium halide directly from the metal and hydrogen chloride gas. In addition, the growth rate which was as high or higher than observed in this work, was related to the hydrogen chloride concentration. This work would suggest that such a variation was due entirely to the changes in the halide formed which depends on the latter factor to a considerable extent.

The results of electrical measurements on layers grown at low temperatures show that the general character of the layers were strongly n-type. This implies the presence of a donor. Extensive analysis of monochloride did not reveal concentrations of likely donors of values higher than 0.1 ppm. Analysis of the phosphine gas proved uncertain. However, it is produced by the reaction of sodium hydroxide and phosphorus. Taking into consideration the nature of the former reagent, there is every likelihood that the phosphine is contaminated with moisture. Water has been previously identified with changes in the electrical characteristics of indium phosphide layers [1] and is again considered to function in the same manner in this system. Much has been made of the function of silicon as a donor in indium phosphide layers [4] although this has not been confirmed [5]. In the present system the formation and transport of silicon as silicon tetrachloride is much less likely considering the reduced amount of hydrogen chloride in the system and also the much lower temperatures of growth. In addition to this there is the possible function of chlorine as an electrically active impurity. Since no crystal system is completely free of the components from which it is produced, the incorporation of chlorine into the layer lattice must be taken as likely. Chlorine would, if electrically active, function as a donor. This work has revealed some evidence for this in that growth in progressively chlorine-rich conditions causes progressive increase in n-type carrier concentration.

The electrical characteristics of layers grown at high temperatures and high growth rates were completely variable. Measurements indicated that not only n-type layers were obtained but also p-type layers were produced. It is possible to attribute these results to the fact that the layers were so inhomogeneous both with respect to inadvertent impurity inclusion or stoichiometry that the measurements were meaningless.

However, careful examination of the results and layer structure did not always reveal effects associated with inhomogeneity shown in Figs. 2 or 6. Thus the change in characteristics stated is taken as a real effect and the presence of an acceptor is required. Photoluminescent examination of these layers stated the acceptor to be zinc [6]. The above results imply that the distribution coefficient for zinc is a strong function of growth rate. Since it is a fundamental rule of crystallization that impurity incorporation increases with increasing growth rate this is not unreasonable. However, there is an alternative explanation which relies on the formation of a greater amount of acceptor at higher temperatures. This is that silicon is an acceptor in the indium–phosphorus epitaxial system. The fact that germanium has been shown to function as an acceptor lends support to this hypothesis [7].

Although the extent of formation of silicon tetrachloride as the source of volatile silicon is much less in this system it is not necessarily negligible and would be more pronounced at high temperatures. This would mean that the proposed donors, the components of water or chlorine, would become progressively more balanced as the growth temperature increased and this would account for the results obtained.

Silicon as an acceptor would be even more relevant to the previous work [1] where it was shown that as conditions were obtained where the formation of silicon became more likely the acceptor photoluminescent spectra [7] improved and the layers became less n-type.

In conclusion this work has shown the reaction between phosphine and indium monochloride is an efficient method of producing epitaxial layers of indium phosphide, over a wide range of temperature and at various growth rates. However, as in previous work, a limitation of reagent purity has been encountered along with difficulty of precise control of growth rates.

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References

1. K. FAIRHURST, D. LEE, D. S. ROBERTSON, H. T. PARFITT and W. H. E. WILGOSS, *J. Mater. Sci.* 16 (1981) 1013.
2. P. J. BORN and D. S. ROBERTSON, *ibid.* 11 (1976) 395.
3. G. JOEL, Deutsche Bundespost Report FTZA18T Br 1 (1968).
4. P. J. DEAN and M. S. SKOLNICK, *J. Appl. Phys.* 54 (1983) 346.
5. C. J. ARMSTEAD, A. M. DAVIDSON, P. KNOWLES, S. P. NAJDA and R. A. STRADLING, "Grenble Proceedings Lecture Notes in Physics" 177 (Springer-Verlag, Berlin, 1982), pp. 289–93.
6. P. J. DEAN, private communication (1983).
7. A. M. WHITE, P. J. DEAN and B. DAY, Rome Semiconductor Conference, Rome, August 1976 (Tyografia Marves 1976, Italy) (North Holland, Amsterdam, 1976) pp. 1057–60.
8. T. E. ERSTFELD and K. P. QUINLAN, *J. Elect. Mater.* 11 (1982) 647.

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