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A study of vapour phase epitaxy of indium phosphide

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The results of a study of the preparation of epitaxial layers of indium phosphide on indium phosphide substrates by means of the PCl_3–In–InP process are presented. The limitations of the process as discovered in this study are described. It is proposed that the major reaction species is phosphine and the unpredictable break-down of this compound, along with the presence of oxyhalides in the phosphorus trihalides, are the significant causes of the observed variation of the parameters of the epitaxial layers.

1. Introduction

Epitaxial layers of indium phosphide were first produced on gallium arsenide by Seki and Kinoshita [1] using the vapour phase reaction between indium, phosphorus trichloride and hydrogen. Such layers were subsequently produced by Joyce *et al.* [2–4] on indium phosphide substrates. Other groups of workers [5–8] have reported on various aspects of the process. During operation of the process it was observed that variations in the growth rate and electrical characteristics of the layers from successive operations were not uncommon and the origin of these variations was examined. The work below describes the results of these experiments and records the likely source of the variations.

2. Experimental procedure

Epitaxial layers were produced using the equipment described in the literature [1, 5]. The system is shown diagrammatically in Fig. 1. It consists of a source of primary reagents (A) which are injected into a horizontally mounted reaction tube (T). The tube is heated in such a manner as to produce two different thermal zones: a reaction zone R and a deposition zone D, by means of the temperature gradients $\underline{a}$ and $\underline{b}$ shown. Zone R is heated to a higher temperature than zone D and contains the secondary reagents required (B). Zone D contains the single-crystal slice on which the required layer is to be produced (S). The primary chemical reagents react with the secondary reagents and the products of this reaction pass into the cooler zone D. In this zone they undergo a further series of reactions and deposit indium phosphide on the crystalline substrate as an epitaxial layer. The products of this reaction condense as solids at C or pass out of the system as gases.

The primary chemical reagents used in this work were phosphorus trichloride and phosphorus tribromide. The secondary chemical reagents were indium metal or solid indium phosphide; the former is liquid at the operating temperatures used. The reagents were used as-obtained from the manufacturers and no further purification was attempted. The hydrogen was purified by palladium diffusion units.

The equipment was cleaned, prepared and operated as previously described [2, 3] with the exception that washing in a 7 parts HF(40%)–2 parts HNO_3(conc.)–7 parts H_2O (by volume) mixture was introduced into the cleaning process, and the whole reaction tube was baked at 750° C in pure hydrogen until the water content of the exit gases fell to 10 ppm. This process often took a week to complete. The single-crystal slices used were cut to within 1° of the desired orientation except for the case of slices cut to expose the (1 0 0) plane for growth. These were cut 2° off this orientation, since it has been established [2] that this is beneficial to the physical quality of the layers. They were polished to a featureless finish before growth by means of mechanical–

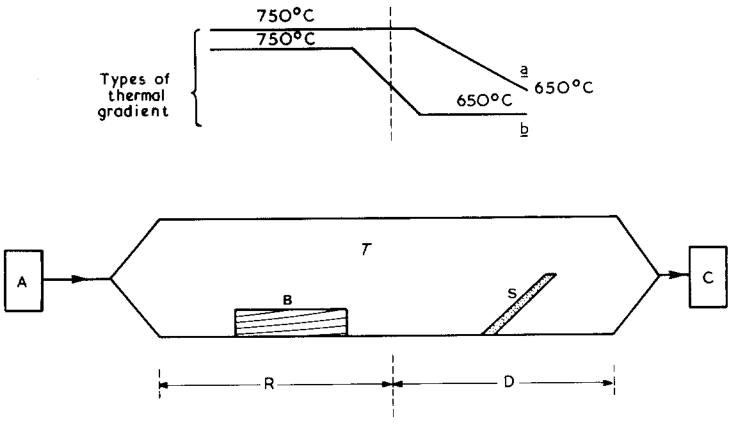

Figure 1 The reaction system used shown diagrammatically.

chemical polishing using 4% bromine : methanol as the chemical polish.

Layer thickness was monitored by cleaving and staining, using the technique of Joel [9], and electrical measurements were made on cloverleaf specimens cut by abrasive machining. These were used for Van der Pauw measurements using specimen currents between 0.02 and 9.2 mA in a permanent magnetic field of 0.15 T. Other electrical measurements were made by *C–V* profiling and device fabrication.

3. Results

Study of the sytem in operation revealed that a very large amount of unreacted products appeared in the condensing region C of Fig. 1. These were analysed as indium monochloride, phosphorus and some indium phosphide. It was also established that using indium metal in zone R and omitting the stage of saturation, whereby a crust of indium phosphide forms on the metal, layer growth was not obtained. Using solid indium phosphide in zone R produced layers readily. Changing the carrier gas from hydrogen to argon or nitrogen resulted in no layer being produced. Using the equipment as described in the literature produced layers and the results of one such series are given in Table I. It can be seen that the growth rate and electrical characteristics vary. The table shows that the results of free electron concentration as measured on conducting substrates, simultaneously grown side by side with layers on

TABLE I

Layer code	Layer thickness (μm)	Electrical properties measured by Van der Pauw				Profile measurements/device at 300 K	
		at 300 K		at 77 K		Carrier concentration	
		Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Sn-doped (cm^{-3})	Cr-doped (cm^{-3})
KV 434	12.0	1.3×10^{15}	5400	1.1×10^{15}	76 200	–	–
KV 435	9.5	3×10^{15}	4300	1.3×10^{15}	60 700	–	–
KV 436	10.5	1.3×10^{15}	5000	9.7×10^{14}	71 600	–	–
KV 438	8.5	6.8×10^{14}	5163	2×10^{14}	10 600	6×10^{13}	5×10^{13}
KV 439	8.4	3.6×10^{14}	4900	9.3×10^{13}	111 400	a 6×10^{13} b 4×10^{12}	5×10^{13}
KV 440	8.0	2.2×10^{14}	5156	1.2×10^{14}	121 050	–	–
KV 441	7.0	3.7×10^{14}	4800	1.7×10^{14}	104 300	a 6.6×10^{14} b 5×10^{13}	7×10^{13}
KV 442	10.0	8.9×10^{14}	5300	7×10^{14}	79 400	–	–
KV 443	10.0	6.6×10^{14}	5219	4.4×10^{14}	88 380	–	–
KV 444	10.0	5×10^{14}	5248	3×10^{14}	82 275	–	–

The metal used was A52314, the temperature used was 750° C and seeded at 650° C (Johnson Matthey Ltd).
The PCl_3 used was B199 mole fraction 1.8×10^{-2} with a gas flow rate of 56 ml min^{-1} (MCP Ltd).
The substrates were Fe doped.
a is the device measurement and b is the profiler measurement.

high-resistivity substrates, are in reasonable agreement with Van der Pauw measurements. This indicates that the latter are acceptable as a measure of electrical properties. Several series were attempted in which all parameters except one were held as constant as possible. It was found that the variations continued when the crystal from which the substrates were obtained was changed, when the positions from which substrate was taken from a given substrate crystal was changed, when the relative temperatures of zones R and D were changed and when the empty reaction tube was cleaned between sequential operations by heating in the trihalide–hydrogen mixture (the same as that used for growth) at 750° C.

It was also established that the dopant used to obtain high resistivity substrates, either chromium or iron, did not affect the results. However, Table II shows that orientation of the substrate did affect the growth rate and electrical characteristics. This table shows that growth on (1 1 1) orientated substrates is faster and the electrical quality is inferior. The two substrates were grown simultaneously side by side. Careful checks of the orientation of the normal (1 0 0) orientated slices showed that variations from the selected orientation were insufficient to account for the variations observed in growth rate and electrical characteristics. Layers with excellent electrical characteristics were etched to reveal dislocations [10]. The results showed that the dislocation content of layers was high, about 7.0×10^4 dislocations cm^{-2} when the electrical characteristics were: mobility $= 5400\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$, $N_e = 1.0 \times 10^{14}\,\text{cm}^{-3}$ at 298 K and mobility $= 111\,000\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$, $N_e = 7.0 \times 10^{13}\,\text{cm}^{-3}$ at 77 K, where N_e is the carrier concentration. Finally, as shown in Table III, variation of the trichloride concentration, produced by varying the temperature and hence the vapour pressure of this reagent, did not reveal any link between growth rate and electrical characteristics and this parameter.

All of the above experiments were performed with indium metal in the reaction zone and gradient a in Fig. 1. The thermal gradient in the equipment was changed to b in Fig. 1, solid indium phosphide was placed in zone R and two slices placed one behind the other in the deposition zone D. The results of layers grown in this way are shown in Table IV: when the temperature in zone R is varied, the layer nearest the source (A) and at the higher temperature grew faster and in addition the electrical characteristics were different between the layers. When the temperature of zone R was progressively increased similar results were obtained but no change in growth rate was observed. These results also indicate that higher growth rates can be obtained by using solid indium phosphide in zone R. The experiments were repeated with indium metal in zone R and the results are given in Table V. Similar effects were observed but the results were not particularly reproducible. It was also observed with increasing reaction zone temperatures and increasing substrate temperatures at A that the growth rate decreased, although little change was seen at B, where the temperature did not change markedly. The weight decrease of solid indium phosphide in zone R was measured per one hour experiment and found to have a mean value, taken from several experiments, of 2.76 g. From the growth conditions listed, it can be seen that changing the samples of metal, but not changing the sample of trichloride, produced equally good electrical characteristics in the layers (Table I and II). The latter also gave good layers using solid indium phosphide. However, using metal from the same series and using a different sample of trichloride (Table V) produced poor electrical characteristics in the layers.

Finally, layers were grown by replacing the phosphorus trichloride with phosphorus tribromide and using solid indium phosphide in the reaction zone. The tribromide is very much less volatile than the trichloride and the pipes linking the tribromide source to the reactor tube had to be heated. Table VI records the results and shows that although layers can be grown the growth rate is lower and, along with the electrical characteristics, varies from experiment to experiment.

4. Discussion

The systems described above exhibit the following characteristics: (1) inefficient reaction in the deposition zone; (2) variations of layer growth rate from preparation to preparation and (3) variations in the electrical characteristics from preparation to preparation.

The first two characteristics are related to the chemical reactions, both in the reaction zone R and the deposition zone D. Calculations of the concentrations of the likely species present under thermodynamic equilibrium have been made [11] and similar calculations made during this work are in agreement. These calculations are strictly

TABLE II

Layer code	Thickness (μm)		Electrical properties measured by Van der Pauw							
			(1 0 0)				(1 1 1)			
			At 300 K		At 77 K		At 300 K		At 77 K	
	(1 0 0)	(1 1 1)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)
KV 348	8.6	22.0	7.8×10^{14}	5017	6.5×10^{14}	103 067	1.8×10^{16}	3813	2.7×10^{16}	4683
KV 349	8.4	20.0	2.9×10^{14}	5154	1.7×10^{14}	101 426	1.4×10^{16}	3349	1.4×10^{16}	6573
KV 350	7.0	19	6×10^{14}	5048	2.9×10^{14}	82 518	3×10^{16}	3698	2.5×10^{16}	6233
KV 353	10.5	21	7.9×10^{14}	5153	6×10^{14}	71 605	6.4×10^{14}	2383	6.1×10^{16}	3339

The metal used was A52078 at 750° C and seeded at 650° C.

The PCl_3 used was B199, mole fraction 1.8×10^{-2} with a gas flow rate of 56 ml min^{-1}.

The substrate was Cr-doped.

TABLE III

Layer code	Layer thickness (μm)	PCl_3 (mole fraction)	Electrical properties as measured by Van der Pauw				Device/ profile technique	
			At 300 K		At 77 K		At 300 K	
			Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($cm^2 V^{-1} sec^{-1}$)	Carrier concentration (cm^{-3})	
							Ge	Fe
KV 462	8.0	9×10^{-3}	5.3×10^{14}	5214	4.7×10^{14}	76 967	–	–
KV 463	7.5	9×10^{-3}	5×10^{14}	5489	5.3×10^{14}	56 878	–	–
KV 464	7.5	9×10^{-3}	1.5×10^{14}	5393	1.8×10^{14}	101 150	7×10^{13}	–
KV 465	7.8	9×10^{-3}	6.7×10^{14}	4854	5.2×10^{14}	68 438	–	–
KV 459	10.0	1.8×10^{-2}	6.5×10^{14}	5272	6.2×10^{14}	85 811	2×10^{14}	–
KV 460	9.0	1.8×10^{-2}	7.2×10^{14}	5626	7.5×10^{14}	81 470	4×10^{13}	–
KV 461	10.0	1.8×10^{-2}	6×10^{14}	5113	6×10^{14}	80 637	–	–
KV 470	8.4	1.8×10^{-2}	2.4×10^{14}	5281	2.4×10^{14}	92 091	–	–
KV 466	10.5	2.8×10^{-2}	1×10^{15}	3419	4.6×10^{14}	67 735	–	–
KV 467	10.2	2.8×10^{-2}	3.7×10^{14}	5348	3.8×10^{14}	86 603	–	–
KV 468	9.0	2.8×10^{-2}	1.5×10^{14}	5325	1.6×10^{14}	92 494	4×10^{13}	4×10^{13}
KV 469	8.5	2.8×10^{-2}	4×10^{14}	5344	4×10^{14}	83 475	–	–
KV 471	8.5	4.8×10^{-2}	High resistivity		High resistivity		–	–
KV 472	6.0	4.8×10^{-2}	High resistivity		High resistivity		–	–
KV 473	10.5	4.8×10^{-2}	High resistivity		High resistivity		–	–
KV 474	10.0	4.8×10^{-2}	High resistivity		High resistivity		–	–
KV 500	8.0	7.6×10^{-2}	1.9×10^{16}	1231	1.9×10^{16}	1 272	–	–
KV 501	5.0	7.6×10^{-2}	1.7×10^{16}	1132	1.2×10^{16}	1 596	–	–
KV 502	5.0	7.6×10^{-2}	1.7×10^{16}	1402	5.9×10^{15}	4 835	–	–
KV 503	6.0	7.6×10^{-2}	4.0×10^{16}	1120	2×10^{16}	2 951	–	–

The metal used was A52314 at 750° C and seeded at 650° C.
The PCl_3 used was B199 with a gas flow rate of 56 ml min^{-1}.
The substrates were Fe doped.

TABLE IV

Layer code	Source temperature (° C)	Seed temperature (° C)		Layer thickness (μm)		Growth rate (μm h^{-1})		Electrical characteristics							
								A				B			
								300 K		77 K		300 K		77 K	
		A	B	A	B	A	B	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})
KV 564	747	679	683	no layers		–	–	–	–	–	–	–	–	–	–
KV 563	744	679	682	8.0	no layer	8.0	–	2.6×10^{15}	922	8×10^{14}	1155	–	–	–	–
KV 554	750	678	674	14.0	14.0	14.0	14.0	3×10^{16}	2536	1.0×10^{16}	15161	8.4×10^{16}	2093	2.8×10^{16}	8377
KV 555	741	667	662	18.0	14.0	18.0	14.0	3.4×10^{15}	4375	2×10^{15}	25977	7×10^{15}	1678	1.4×10^{15}	12231
KV 556	739	663	656	21.0	15.0	21.0	15.0	1.4×10^{15}	4505	8×10^{14}	25466	1×10^{15}	1512	7.3×10^{13}	18667
KV 557	742	664	652	26.0	12.0	26.0	12.0	4×10^{14}	4217	1×10^{14}	26817	3.6×10^{15}	1331	4.5×10^{14}	12750
KV 558	743	662	649	21.0	18.0	21.0	18.0	1.2×10^{15}	1105	2.3×10^{14}	2250	1.5×10^{16}	67	6.8×10^{15}	52
KV 559	743	660	641	21.0	14.0	21.0	14.0	2.5×10^{15}	718	3.3×10^{15}	139	2.1×10^{15}	357	High resistance	
KV 560	749	657	629	20.0	14.0	20.0	14.0	2.7×10^{15}	674	9.5×10^{14}	594	6.9×10^{15}	429	4.2×10^{15}	462
KV 561	744	649	617	35.0	23.0	35.0	23.0	9.5×10^{15}	1284	4.9×10^{15}	1772	1.6×10^{16}	876	1.2×10^{16}	848
KV 562	743	645	614	30.0	16.0	30.0	16.0	5×10^{15}	1841	2.8×10^{15}	2535	5×10^{16}	898	3.7×10^{16}	1010
KV 584	742	663	658	14.0	9.0	14.0	9.0	1.9×10^{16}	2437	9.9×10^{15}	13189	4.9×10^{15}	4531	5.7×10^{14}	38054
KV 609	747	673	653	15.3	8.7	15.3	8.7	8.7×10^{15}	2490	2.4×10^{15}	19063	2.1×10^{15}	3399	1.1×10^{15}	24460
KV 610	748	672	652	16.7	7.9	16.7	7.9	2.4×10^{15}	3169	1.1×10^{15}	24821	7.6×10^{14}	4237	6.3×10^{13}	41614
KV 611	749	673	651	14.2	7.0	14.2	7.0	4.9×10^{15}	3515	1.2×10^{14}	28407	2×10^{14}	1489	3.1×10^{12}	30677
KV 585	791	691	660	14.0	7.3	14.0	7.3	4×10^{16}	1897	8.8×10^{15}	14958	8.9×10^{15}	2593	1.5×10^{15}	29382
KV 586	840	718	660	14.7	8.8	14.7	8.8	2.5×10^{16}	2454	1.3×10^{16}	16054	6.5×10^{15}	3800	3.3×10^{15}	47742

The source used was solid InP.

The PCl_3 used was B199 and mole fraction of 4.6×10^{-2} with a gas flow of 66 ml min^{-1}.

A = 5 cm from source.

B = 13 cm from source.

TABLE V

Layer code	Temperatures (° C)			Layer thickness (μm)		Electrical characteristics							
	Source	Substrates				300 K				77 K			
		A	B	A	B	A		B		A		B	
						$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})	$N_D - N_A$ (cm^{-3})	μ (cm^2 V^{-1} sec^{-1})
KV 569	746	672	676	2.0	4.0	3.6×10^{15}	3347	3.7×10^{16}	1478	1.9×10^{15}	1530	1.7×10^{16}	2719
KV 565	748	667	662	5.0	2.5	1×10^{16}	2545	5.6×10^{15}	3001	3.6×10^{15}	8353	1.2×10^{16}	22900
KV 566	747	662	653	5.0	2.0	3.2×10^{16}	1306	1.2×10^{16}	763	2.3×10^{16}	1600	3.7×10^{15}	800
KV 567	747	656	643	5.0	2.0	1.4×10^{16}	1611	1×10^{16}	1026	1.4×10^{15}	18400	1.4×10^{15}	681
KV 568	748	652	632	4.0	1.0	2.6×10^{16}	1360	1.6×10^{17}	124	2.2×10^{16}	1228	High resistance	
KV 579	600	590	659	No layer	Etched	–	–	–	–	–	–	–	–
KV 578	662	622	659	7.0	No layer	8×10^{16}	948	No layer		8×10^{16}	825	–	–
KV 580	700	642	660	3.5	No layer	4×10^{16}	1956	No layer		2×10^{16}	3500	–	–
KV 571	778	651	658	6.0	4.0	7×10^{17}	2480	1.3×10^{17}	3366	6.8×10^{17}	2199	9×10^{16}	4778
KV 572	776	676	649	4.0	5.0	5.8×10^{15}	3191	4×10^{16}	1873	1.9×10^{15}	16172	1×10^{16}	8728
KV 574	798	704	662	6.0	4.5	5×10^{16}	2134	6×10^{15}	3810	2×10^{16}	9300	3×10^{15}	20200
KV 575	830	710	663	4.0	5.0	1×10^{17}	2400	1×10^{16}	4353	4×10^{16}	7532	8×10^{15}	16900
KV 576	852	725	661	2.5	6.0	1×10^{17}	2600	2×10^{16}	3900	6×10^{16}	5600	1×10^{16}	11874
KV 577	879	742	661	1.0	7.0	1×10^{15}	1600	5×10^{16}	2700	7×10^{17}	2400	2×10^{16}	900

The metal used was A52376.
The PCl_3 used was B195 and mole fraction of 4.6×10^{-2} with a gas flow rate of 56 ml min^{-1}.
A = 5 cm from source.
B = 13 cm from source.

TABLE VI

Layer code	Source temperature (° C)	Substrate temperature (° C)	Layer thickness (μm)	Electrical properties			
				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})
KV 659	847	645	4.7	1.0×10^{15}	1542	6.5×10^{14}	8663
KV 660	847	644	3.5	High resistivity			
KV 661	847	646	2.0	High resistivity			
KV 662	847	647	2.6	6.2×10^{15}	1513	4.0×10^{15}	1517
KV 663	898	647	2.5	High resistivity			
KV 664	746	546	3.7	2.4×10^{16}	1423	2.1×10^{16}	1478

Hydrogen flow rate = 100 cm^3 min^{-1}.
PBr_3 mole fraction = 3.5×10^{-2}.

applicable when only one condensed phase is present in the reaction zone, i.e. indium phosphide. The species present and their concentrations under the conditions used in the reaction zone during this work in order of descending concentration are indium monochloride, tetrameric phosphorus, dimeric phosphorus, hydrogen chloride, phosphine and possibly indium dichloride. Using the values obtained the rate of weight loss of a solid piece of indium phosphide in the reaction zone and further the likely deposition rate of indium phosphide on a 1 cm^2 slice of crystal in the deposition zone can be calculated. The results are shown in Fig. 2. This shows the weight loss expected at 750° C, the usual temperature of the reaction zone in this work, to be about 3.0 g per hour long experiment. The measured value was 2.76 g and hence this indicates equilibrium conditions could exist in the reaction zone. However, it must be noted that the measured value is a mean value and the variations found indicate that complete equilibrium need not be attained on every occasion. The results also indicate that transport of such an amount of material would produce a growth rate of 2100 μm h^{-1}. However, it is evident that this does not happen since the forming indium phosphide has alternative surfaces for deposition. Reducing this by a factor of 70 by assuming an even deposition over all the surface available in the deposition zone (internal diameter 23 mm, length 100 mm) a growth rate of 30 μm h^{-1} would be expected.

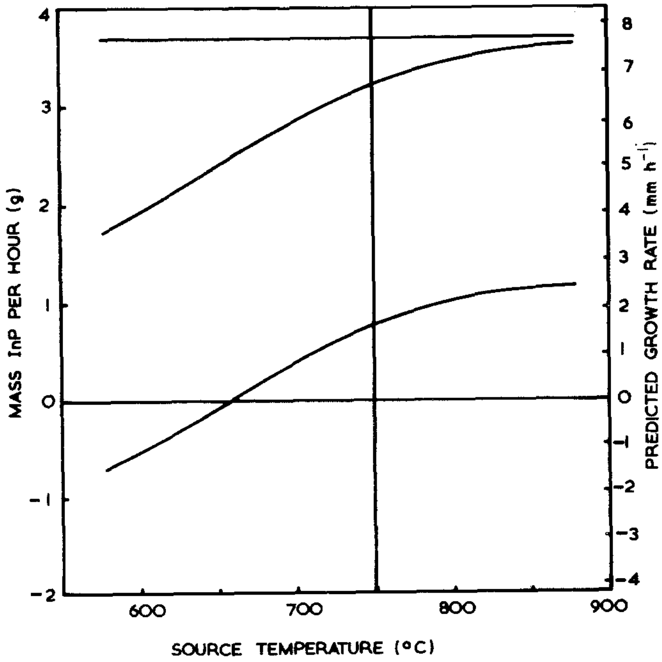

Figure 2 Theoretical derivation of transport and growth.

Finally, the calculations predict that as the reaction zone temperature alone increases the rate of growth should reach a maximum.

None of these predictions is confirmed by the results presented in Tables IV or V. The results do indicate that higher growth rates are attainable using solid indium phosphide, and that for indium metal sources at least, the growth rate slows down as temperatures of the substrate in excess of 700° C are reached. Both observations are recorded in the literature [12]. The observation that the substrate in the hottest position generally grew faster is also not in accord with thermodynamic considerations. Finally, uniform deposition of indium phosphide over all the interior of the deposition zone was not a usual occurrence. This indicates that very much less of this compound was being formed than was expected.

The assumption made regarding reactions in the deposition zone is that the species present in major amounts, namely indium monochloride and tetrameric phosphorus undergo reaction. However, this reaction has been tested independently [13] and found not to be efficient. Taking the results given into account, this assumption is not necessarily valid.

An alternative explanation is that the reaction in the deposition zone is solely between phosphine and indium monochloride. The presence of phosphine in these reactors has been proved as well as predicted and the amounts have been shown to be higher than calculated [14, 15]. Again the reaction between phosphine and indium monochloride has been tested independently and found to be efficient [13]. Finally, it has been shown that hydrogen is an integral part of the reaction. When involving phosphine there are two possibilities for reaction in the reaction zone, namely, those envisaged from thermodynamic calculations and

$$PCl_3 + 3InP + 6H_2 \rightarrow 4PH_3 + 3InCl. \quad (1)$$

The latter would lead to very much more phosphine being present than calculated as apparently observed. When the phosphine enters the deposition zone it undergoes two reactions

$$2PH_3 \rightarrow P_2 + 3H_2 \quad (2)$$

and

$$PH_3 + InCl \rightarrow InP + HCl + H_2. \quad (3)$$

The dimeric phosphorus formed from Equation 2 will associate and give tetrameric phosphorus which since it does not react will be deposited in the deposition zone C. This dissociation reaction of phosphine has been studied [16–18] and the results indicate that the reaction may take place through a chain mechanism, and is affected by the nature of surfaces present and the presence of moisture and inert gases. It has been further recorded that the reaction with moisture is catalysed by the presence of metals and phosphides [19]. Thus, the extent of Equation 3, which controls the layer growth rate, is dependent on the extent of Equation 2. The latter is unpredictable and hence the growth rate is unpredictable, as observed during this work. Thus, the condensation of unreacted indium monochloride is to be expected and is found. This postulation of phosphine as the major reaction species has two consequences. The first is that it could lead to variations in stoichiometry in the layers and hence to variations in electrical properties. The second is that as the deposition zone temperature is progressively raised the tendency for Equation 2 to take place will increase and hence the layer growth rate will decrease. This effect has been observed [12].

With respect to the variation of electrical characteristics, it has been demonstrated during this work that a source of variation in the electrical characteristics was changes in the sample of trichloride used. Thus the trichloride was examined and found to contain up to 500 ppm of phospherus oxychloride [20]. This compound has a vapour pressure similar to that of phosphorus trichloride and in the reaction zone would result in the formation of water. Water would interfere with the chemical reactions and has been shown to affect the electrical characteristics of epitaxial layers of indium phosphide [21]. Changes in water concentration, due to variation of the trichloride concentration, could also account for an effect recorded in the literature, where high concentrations of trichloride produced layers with low electron concentrations [5, 8]. However, this effect was not observed with one of the samples of trichloride used and was not confirmed by results for the second sample. Nevertheless, the differences observed in this work are still explained by moisture originating from the oxychloride. This is further indicated by the fact that after careful drying of the system, the electrical characteristics were initially reasonable and tended to degenerate with time; the latter effect being a result of the system being progressively contaminated with moisture from the oxychloride, and the different results from each trichloride sample being due to different oxychloride content.

It is worth noting here that the contaminating ions which arise from water are O^{2-} and OH^-. The former would be a donor impurity if it entered the lattice substitutionally and the latter could be an isoelectronic impurity under the same conditions. Thus, if both entered the lattice simultaneously then both the free electron concentration and the electron mobility would be affected. This was often observed during this work in layers with a free electron concentration of $10^{12}\,cm^{-3}$ and a mobility of only 20 000 $cm^2\,V^{-1}\,sec^{-1}$ at 77 K. Such layers are electronically different from those quoted in this work and could be involved in some results in the literature.

Variations of electrical characteristics could also result from inclusions of halide ions into the lattice. However, the similarity in electrical characteristics obtainable by both trichloride and tribromide, despite the difference in ion size between bromide and chloride which would suggest a difference in the ability to enter the lattice, makes this unlikely.

In conclusion, the results presented strongly indicate that variations of growth rate and chemical inefficiency in the system described for the preparation of epitaxial layers of indium phosphide probably result from the unpredictable break-down of the proposed main reacting species, phosphine. The variations of electrical characteristics are considered to result from contamination of the system with water mainly originating from oxychloride in the phosphorus trichloride. Even if the latter could be eliminated, and hence more consistent electrical results attained, the chemical inefficiency of the system cannot be improved.

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References

1. H. SEKI and M. KINOSHITA, *Jap. J. Appl. Phys.* **7** (1968) 1142.
2. B. D. JOYCE, R. G. CLARKE and W. H. E. WILGOSS, *Sol. State. Comm.* **8** (1970) 1125.
3. B. D. JOYCE and E. W. WILLIAMS, *Inst. Phys. Conf. Series* **9** (1970) 57.
4. B. D. JOYCE, K. M. FAIRHURST, R. C. CLARKE and P. J. BORN, *J. Cryst. Growth* **11** (1971) 243.
5. R. C. CLARKE, *ibid.* **23** (1974) 166.
6. R. C. CLARKE and L. L. TAYLOR, *ibid.* **43** (1978) 473.
7. R. D. FAIRMAN, M. OMORI and F. B. FANK, *Inst. Phys. Conf. Series* **33B** (1977) 45.
8. J. CHEVRIER, A. HUBER and N. T. LITH, *J. Cryst. Growth* **47** (1979) 267.
9. G. JOEL, Deutsche Bundespost Report FTZA18T Br 1 (1968).
10. R. C. CLARKE, D. S. ROBERTSON and A. W. VERE, *J. Mater. Sci.* **18** (1973) 1349.
11. D. W. SHAW, *J. Phys. Chem. Sol.* **36** (1975) 111.
12. O. MIZUNO, *Jap. J. Appl. Phys.* **14** (1975) 451.
13. P. J. BORN and D. S. ROBERTSON, *J. Mater. Sci.* **11** (1976) 395.
14. V. S. BAN, *J. Electro. Chem. Soc.* **118** (1971) 1473.
15. *Idem, J. Cryst. Growth* **17** (1972) 19.
16. R. H. DALTON, *Proc. Roy. Soc.* **128** (1930) 263.
17. C. N. HINSHELWOOD and B. TOPLEY, *J. Chem. Soc.* **125** (1924) 393.
18. M. TRAUTZ and W. GABLER, *Z. Anorg. Chem.* **180** (1929) 321.
19. I. N. BUSHINAKIN and A. V. FROST, *J. Appl. Chem. (USSR)* **6** (1933) 607.
20. M. CARDWELL, M. C. HALES, D. C. NEWTON, P. L. GILES and J. A. SPARROW, Plessey Co Ltd, England, private communication (1977).
21. M. C. HALES and J. R. KNIGHT, *J. Cryst. Growth* **46** (1979) 582.

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