
**EQUILIBRIA IN THE TRANSPORT EPITAXIAL FORMATION
OF INDIUM PHOSPHIDE AND ARSENIDE***

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Received May 15th, 1984

From the data available in literature, equilibria were calculated of the reactions which come into consideration in the preparation of indium phosphide and indium arsenide. In the first case it was supposed that indium phosphide was formed as a pure solid substance, that indium might exist either as a pure liquid, or as a gas and that the remaining 16 components in the equilibrium mixture were in the ideal gaseous state. In the second case, the formation of pure solid indium arsenide and the existence of 18 other substances in the equilibrium mixture, also in the ideal gaseous state, were supposed. The results of these theoretical calculations for indium phosphide were compared with the experimental deposition temperatures and reasonable agreement has been found.

The significance of the substances of the A(III)B(V)-type having their origin in epitaxial changes has enormously grown in recent years; to this family of substances belong among others the compounds InP and InAs. Besides experimental studies devoted to the preparation of these compounds there exists in the literature a number of theoretical papers dedicated to the calculation of equilibria and to the investigation of conditions under which these substances can be formed (see, e.g.^{1,2}); however, these theoretical studies are subject to certain *a priori* ideas about the course of chemical reactions leading to the deposition of indium phosphide or arsenide from the gas phase or about the number of substances present in the equilibrium mixture; therefore, we have carried out calculations of equilibrium compositions for a wide range of temperatures which have to be considered in connection with the deposition of solid indium phosphide and arsenide. In these calculations we considered almost all the substances that can exist in the corresponding equilibrium mixtures.

The growth of epitaxial layers of indium phosphide has also been investigated experimentally. In a flow apparatus the deposition temperature as well as further data of this substance were determined as functions of input parameters.

* Part IX in the series Chemical Equilibria in Heterogeneous Systems; Part VIII: This Journal 46, 3157 (1981).

THEORETICAL

The procedure used for the calculation of chemical equilibrium is based on the minimization of the total Gibbs energy of the system in question by the method of Lagrange multipliers. Computations have been carried out on the computer Hewlett-Packard 2116 B.

The substances which can exist in the systems in question are given in Table I, together with the corresponding thermodynamics data. More detailed data, the method of their selection, and/or of their calculation are available on request.

TABLE I
Thermochemical data of substances in the In-H-Cl-P and In-H-Cl-As systems

Substance ^a	$-[G^0(T) - H^0(298.15 \text{ K})]/T, \text{ J K}^{-1} \text{ mol}^{-1}$			$\Delta H_f^0(298.15 \text{ K}), \text{ kJ mol}^{-1}$
	400°C	650°C	900°C	
In (l)	68.2	75.1	81.0	3.26
In	179.3	183.6	187.7	243.3
H ₂	138.0	143.8	148.9	0
H	120.0	124.0	127.6	217.97
Cl ₂	232.0	239.1	245.3	0
Cl	170.8	175.3	179.1	121.68
HCl	194.3	200.1	205.2	-92.31
InCl	256.2	262.8	268.7	-69.9
InCl ₃	364.5	380.0	393.7	-380.0
In ₂ Cl ₃	374.9	392.6	408.2	-439.7
In ₂ Cl ₄	485.5	507.6	527.2	-591 ± 12
In ₂ Cl ₆	590.7	621.7	649.1	-880.3
P	168.4	172.5	176.0	316.4
P ₂	226.7	233.5	239.5	144.3
P ₄	298.6	313.5	326.9	58.91
PH ₃	221.0	230.5	239.5	5.44 ± 1.7
PCl ₃	330.9	346.3	359.9	-287.0
InP (s)	72.1	81.8	90.4	-78.7
As	179.5	183.7	187.1	286.0 ± 6.7
As ₂	248.5	255.6	261.9	190.5 ± 2.1
As ₄	334.3	350.1	364.1	156.2 ± 0.8
AsH ₃	233.8	243.6	252.0	66.44
AsCl	286.4	293.6	300.0	177 ± 12
AsCl ₂	315.6	326.7	336.4	-62.8 ± 17.0
AsCl ₃	346.4	362.0	375.8	-268 ± 8
InAs (s)	88.8	99.2	108.5	-64.0 ± 4.0

^a Unless otherwise stated, all substances are in the ideal gaseous state.

Equilibria in the System In-H-Cl-P

The calculations of chemical equilibria in this system have been performed under the assumption that indium phosphide is formed as a pure crystalline substance and all other substances behave as ideal gases at all the temperatures and at a pressure of 101·325 kPa.

The equilibrium calculations have been carried out for the temperature range 400 to 900°C and for 15 variants of input composition; in Figs 1 through 3, the equilibrium compositions are shown graphically for three selected variants.

The results of these calculations lead to the following conclusions for the formation of solid indium phosphide:

1. At 400 and 500°C, solid InP is formed for all the variants of input composition; starting with the temperature of 750°C, InP(s) does not arise in any case.

2. The rise of temperature causes in all cases the drop in the yield of solid indium phosphide; so, for example, in the case of the variant shown in Fig. 2, the conversion

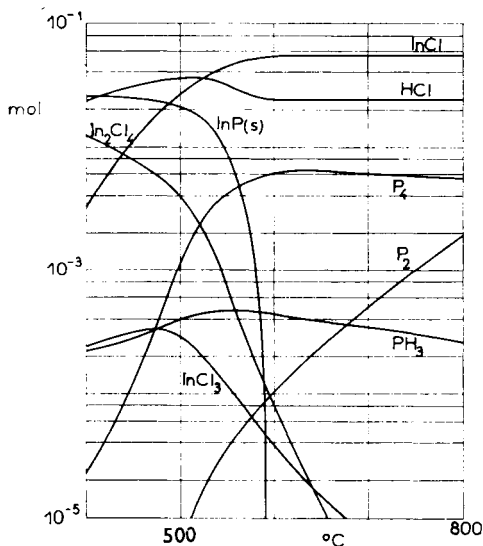


FIG. 1

Calculated equilibrium composition in the In-H-Cl-P system as a function of temperature (the amount of hydrogen is not drawn; it remains practically constant in the whole temperature interval, *i.e.* 0·90 mol). Amounts of initial species (mol) In: $5\cdot50 \cdot 10^{-2}$, H_2 : 0·8400, HCl: $7\cdot90 \cdot 10^{-2}$, PH_3 : $2\cdot60 \cdot 10^{-2}$

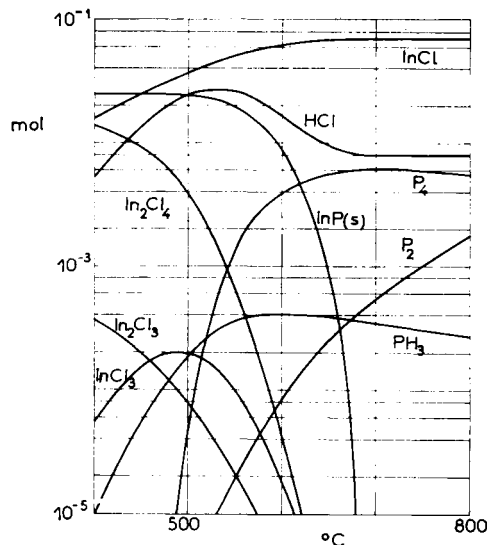


FIG. 2

Calculated equilibrium composition in the In-H-Cl-P system as a function of temperature (the amount of hydrogen is not drawn; it remains practically constant in the whole temperature interval, *i.e.* 0·90 mol). Amounts of initial species (mol) In: $6\cdot90 \cdot 10^{-2}$, H_2 : 0·8290, HCl: $7\cdot70 \cdot 10^{-2}$, PH_3 : $2\cdot50 \cdot 10^{-2}$

of indium to InP (s) at 450°C is equal to 85.6%, at 650°C only to 4.2%. The comparison of the results of calculations for individual variants leads to the conclusion that the value of the deposition temperature is predominantly influenced by the molar ratio $n(\text{In})/n(\text{Cl})$ at the entrance to the deposition zone. The value of this ratio depends on the reactions taking place in the source zone and there the dominating reaction is



3. The concentrations of In , PCl_3 , H , Cl_2 , Cl and P in the equilibrium gaseous mixture are negligible in comparison with the contents of other components at all experimental temperatures.

4. At the lowest temperatures, indium is present in the gaseous phase mainly as InCl , InCl_3 , In_2Cl_3 and In_2Cl_4 ; at the highest experimental temperatures, practically all indium in the gas is present as InCl .

This series of calculation has been extended in the following directions:

a) Equilibria in the gaseous system In-H-Cl for three variants of input composition and in the temperature range 400 to 800°C have been calculated.

b) Equilibria in the In-H-Cl system, where indium can exist in both, liquid and gaseous state have been calculated. These calculations have been performed for 7 variants of input composition and for the temperature interval 400 to 900°C .

The purpose of both these additional sets of calculations was to yield more detailed information on the behaviour of the system under investigation at extreme conditions,

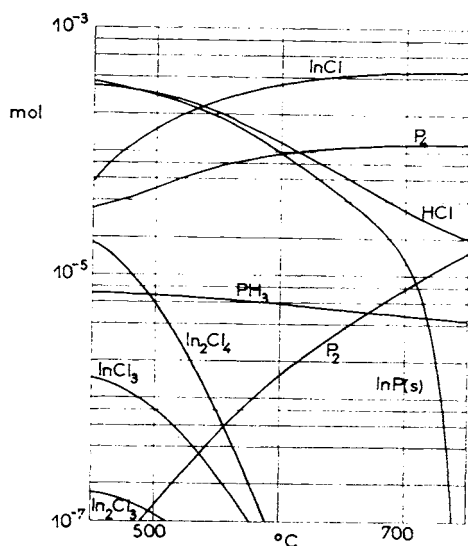


FIG. 3

Calculated equilibrium composition in the In-H-Cl-P system as a function of temperature (the amount of hydrogen is not drawn; it remains practically constant in the whole temperature interval, *i.e.* 10^{-2} mol). Amounts of initial species (mol) InCl : $4.5 \cdot 10^{-4}$, H_2 : $1 \cdot 10^{-2}$, HCl : $2 \cdot 10^{-5}$, PH_3 : $5 \cdot 10^{-4}$.

namely in the case of the absence of phosphorus compounds (case *a*)) and in the case when liquid indium is present which in a real case always exists in the source zone in excess (case *b*)). The results of these calculations led to the following conclusions:

c) The contents of In, H, Cl₂ and Cl in the equilibrium gaseous mixture is at all experimental temperatures negligible when compared with the contents of other substances. At the lowest temperatures, indium is present predominantly as InCl and In₂Cl₄ but in a not negligible quantity also as InCl₃, In₂Cl₃ and In₂Cl₆; at the highest temperatures, almost all indium is present as InCl.

d) If the ratios of the amounts of substances in the input mixture are of the following values $n(\text{In})/n(\text{Cl}) < 0.9$ and/or $n(\text{H}_2)/n(\text{HCl}) > 10$, no liquid indium is deposited in the temperature interval under investigation; in the case that $n(\text{In})/n(\text{Cl}) = 2.2$, liquid indium is present at all experimental temperatures.

Equilibria in the System In-H-Cl-As

The calculations of chemical equilibria in this system have been performed under analogous assumptions as in the case of the system In-H-Cl-P, *i.e.*: indium arsenide was supposed to arise as a pure crystalline substance and ideal behaviour of all the substances in the gaseous state was expected.

The calculations of equilibrium compositions have been performed for the temperature range 400 to 900°C and for eight variants of input composition; in Figs 4

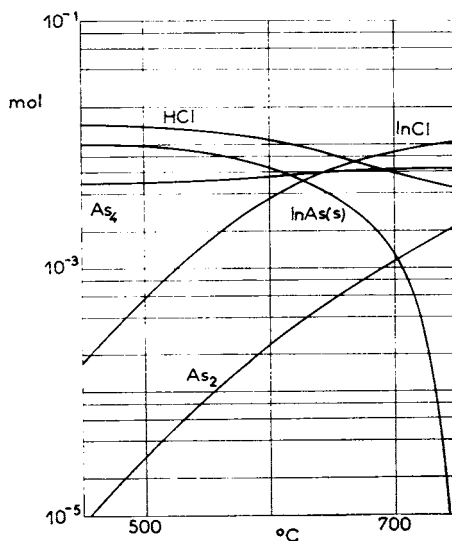


FIG. 4

Calculated equilibrium composition in the In-H-Cl-As system as a function of temperature (the amount of hydrogen is not drawn; it remains practically constant in the whole temperature interval, *i.e.* 0.99 mol). Amounts of initial species (mol) In: $1.024 \cdot 10^{-2}$, H₂: 0.9459, HCl: $1.463 \cdot 10^{-2}$, AsH₃: $2.926 \cdot 10^{-2}$

through 6, the equilibrium composition is shown graphically for three selected variants.

The results of these calculations lead to the following conclusions for the formation of solid indium arsenide:

1. In the temperature interval 400 to 700°C, solid InAs is formed for all the variants of input composition; in contradistinction to indium phosphide, the deposition temperature of indium arsenide may be higher than 750°C; a suitable choice of the input composition leads to the deposition of solid indium arsenide even at 900°C.

2. The temperature rise causes in all cases the drop in the yield of solid indium arsenide; so, for example, in the case of the variant shown in Fig. 4, the conversion of indium to InAs (s) at 400°C is equal to 37.0%, at 800°C only to 3.4% and in the case of the variant shown in Fig. 6 this conversion amounts to 99.6% at the temperature of 400°C, whereas at 900°C it drops to only 0.4%.

3. The contents of In, AsCl, AsCl₂, AsCl₃, H, Cl₂, Cl and As in the equilibrium gaseous mixture at the lower temperatures is negligibly small; at high temperatures,

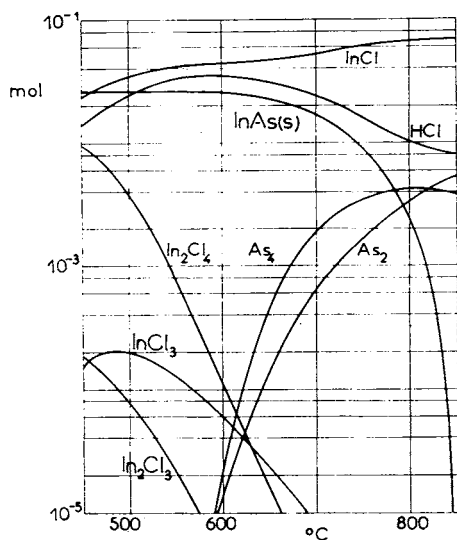


FIG. 5

Calculated equilibrium composition in the In-H-Cl-As system as a function of temperature (the amount of hydrogen is not drawn; it remains practically constant in the whole temperature interval, *i.e.* 0.90 mol). Amounts of initial species (mol) In: $6.917 \cdot 10^{-2}$, H₂: 0.8283, HCl: $7.686 \cdot 10^{-2}$, AsH₃: $2.562 \cdot 10^{-2}$

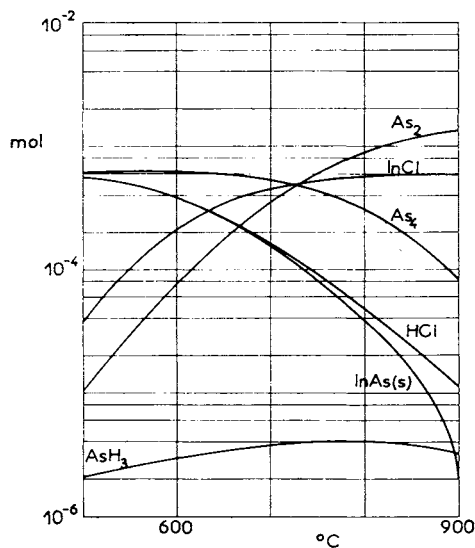


FIG. 6

Calculated equilibrium composition in the In-H-As-Cl system as a function of temperature (the amount of hydrogen is not drawn; it remains practically constant in the whole temperature interval, *i.e.* 1.0 mol). Amounts of initial species (mol) In: $5.933 \cdot 10^{-4}$, H₂: 0.9958, HCl: $5.993 \cdot 10^{-4}$, AsH₃: $2.996 \cdot 10^{-3}$

this statement holds true for all the above-mentioned species with the exception of In and H, the concentration of which in the equilibrium mixture represent even more than approximately 10% of the solid indium arsenide formed.

4. At the lowest temperatures, indium is present in the gaseous phase predominantly as InCl , InCl_3 , In_2Cl_3 and In_2Cl_4 ; at the highest temperatures, practically all indium in the gas phase is in the form of element and of InCl .

EXPERIMENTAL

In order to verify the rightness of the chosen thermodynamic model, the deposition temperatures for some selected systems In–H–Cl–P have been experimentally determined. This temperature may be defined as the highest temperature at which in the given gaseous system the deposition of the first infinitesimal quantity of the solid phase takes place. The experimental determination has been made visually, *i.e.* the temperature has been determined at which the first observable layer of the solid product on the substrate was formed. According to our rough estimate this first visually observable amount of the deposited solid phase is of the order of 10^{-6} to 10^{-5} mol.

The experimental investigation of the formation of epitaxial layers has been performed in the apparatus sketched in Fig. 7; the apparatus has been heated with a three-zone resistance furnace. In the first series of experiments we have introduced phosphorus trichloride in the stream of hydrogen as carrier gas on the surface of liquid indium, placed in the first zone of the reactor (so-called source zone). This so-called chloride method proved to be not suitable for two reasons: firstly, a layer of the phosphide InP has been formed on the liquid indium changing thus the size of the source's surface and so diminishing the reproducibility of the whole process; secondly, this procedure seriously limited the possibility of choice of the mutual ratio of elements of the third and fifth group in the gaseous mixture leaving the source zone. Therefore, the so-called hydride method has been used for the preparation of indium phosphide layers as well as for the determination of its deposition temperatures.

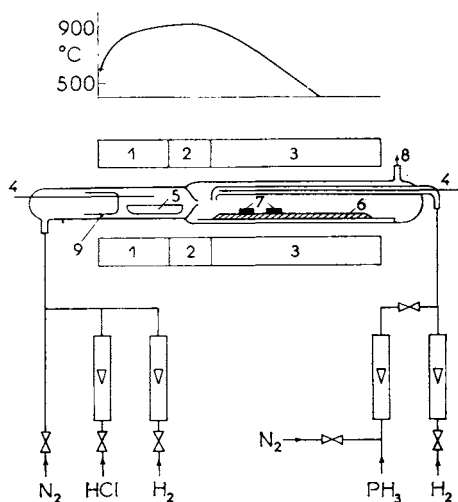


FIG. 7

Apparatus used for the preparation of indium phosphide layers by epitaxial growth from the gas phase. 1, 2, 3 three-zone furnace, 4 thermocouples, 5 liquid indium, 6 support, 7 substrate, 8 exhaust, 9 quartz insertion; in the upper part, the temperature profile of the furnace is shown

In the experiments using the hydride method, a mixture of hydrogen and of hydrogen chloride has been introduced on the surface of liquid indium in the source zone. The reaction tube was constructed in such a way that the source of indium was separated from the deposition zone by means of a partition with a small hole (diameter 2 mm) and from the supply of the H_2 -HCl mixture by a quartz insertion the purpose of which was to limit the deposition and accumulation of solid indium chlorides in the colder part before the source zone. The area of the indium source's surface was 30 cm^2 and its temperature amounted to 900°C . The increase of the surface area and the temperature rise would, of course, increase the indium conversion in its reaction with hydrogen chloride but, at the same time, would make unreasonable demands on the size of the apparatus and would lead to the lowering of the furnace's service life. As follows from a series of experiments, the molar ratio In/Cl under the above-mentioned experimental conditions has been within the limits 0.92 and 0.97. This value has been ascertained on the basis of the determination of indium decrease by weighing and from the known amount of hydrogen chloride passed through the apparatus. Phosphorus has been introduced as phosphine; the mixture of hydrogen with 5 mole% of PH_3 was led by a long tube ended by a jet through the whole length of the reactor from its end to the mixing zone. The preheated mixture of PH_3 and H_2 entered here perpendicularly into the stream of the gaseous mixture leaving the source zone, thus ensuring a thorough mixing of both streams. In the next part of the reactor, *i.e.* in the part of decreasing temperature, the formation of the solid phase InP took place. The temperature profile of the reactor has been determined during each experiment. The gases have been dosed by means of the flowmeters manufactured by Krohne Co. which enabled to measure the minimum values of flow rate of $5 \cdot 10^{-4}\text{ mol min}^{-1}$ in the case of HCl and $1 \cdot 10^{-4}\text{ mol min}^{-1}$ in the case of PH_3 . It has been possible to change the value of molar ratio In/P within the interval 0.25 to 2.

After each experiment, the apparatus was thoroughly rinsed with nitrogen to prevent the self-ignition of phosphorus formed and to avoid a contingent explosion of the mixture of hydrogen present in the apparatus and of oxygen from the air.

RESULTS AND DISCUSSION

As stated above, we compared the results of the theoretical calculations with the values of experimentally determined deposition temperatures in the case of the system In-H-Cl-P. It would be, of course, possible to analyze the gaseous mixture during the experiment but such a procedure would be very expensive and the results obtained in this way would not justify the inevitable cost and efforts.

On the basis of a series of experiments, the values of deposition temperature have been compared for a system with the value of molar ratio In/Cl equal to 0.9. The experimental values of deposition temperature ranged from 650 to 720°C . The value calculated for an analogous system is lower than 700°C , approximately 680°C (see Fig. 2). Furthermore, an experiment has been performed the parameters of which corresponded approximately to the input values in the theoretical calculation with the results shown in Fig. 3; the deposition temperature found experimentally was about 720°C . The calculation led to the value lower than 750°C , approximately 740°C .

The dependence of the value of deposition temperature on the value of molar ratio In/Cl has been investigated only on a qualitative level. It has been found that

the decrease of temperature in the source zone which is accompanied by the diminishing of the value of ratio In/Cl leads to a simultaneous decrease of the deposition temperature. This dependence found experimentally is also in accordance with theoretical calculations the results of which are shown in Figs 1 through 3.

In a similar way the change of the deposition temperature caused by the change of the phosphine amount in the initial mixture was investigated. This effect was probably so small that with the contemporaneous reproducibility of experiments and for the range of feed rates of phosphine used ($5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ mol min $^{-1}$) it was undetectable. Even this result is in qualitative agreement with the results of theoretical calculations.

REFERENCES

1. Shaw D. W.: *J. Phys. Chem. Solids* **36**, 111 (1975).
2. Jones K. A.: *J. Cryst. Growth* **60**, 313 (1982).

Translated by the author (Č. Č.).