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## THERMODYNAMIC STUDIES OF THE SILICON TRANSPORT IN LPE GROWTH ON InP SUBSTRATES

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**Résumé :** L'origine de l'impureté Si dans les semi-conducteurs à base de InP/InGaAsP, élaborés par épitaxie en phase liquide, a été étudiée par le calcul thermodynamique des équilibres complexes existant dans un réacteur classique : tube en quartz, nacelle en graphite et atmosphère d'hydrogène. Le silicium se trouve essentiellement sous la forme des molécules  $\text{SiH}_4$ ,  $\text{SiO}$  et  $\text{SiP}_2$ , en phase gazeuse

et du carbure SiC en phase condensée. Lorsque le flux d'hydrogène est porteur de vapeur d'eau, les teneurs en silicium de la phase gazeuse diminuent, et le SiC disparaît. Les calculs thermodynamiques prévoient les dopages ou purifications en silicium des substrats InP. Les résultats obtenus expliquent les observations expérimentales. La même approche a été utilisée pour étudier le rôle de la phosphine.

**Abstract :** Thermodynamic calculations are used to investigate the transport processes in a conventional LPE growth reactor on InP substrate. The influence of the furnace materials, silica tube and graphite boat, are analysed during the two main operations : baking and growth. The silicon is carried by  $\text{SiH}_4$ ,  $\text{SiO}$

and  $\text{SiP}_2$  molecules and we have calculated the doping of InP substrates with silicon. The experimental determinations are in agreement with our calculations as well as for phosphine concentrations in the  $\text{H}_2$  carrier gas than for the Si impurity concentrations without baking and after baking with small  $\text{H}_2\text{O}$  vapor content in  $\text{H}_2$ .

**1. Introduction.** - The silicon impurity in the InP and InGaAsP compounds may originate from two sources : the Si contained in the In metal base either for the In baths or for elaboration of InP substrates, and the silicon which may be transported in the LPE reactors after the  $\text{H}_2$  attack of the silica tube.

The silicon which is contained in the metallic In basic constituent has a concentration of about 0.1 to 0.03 p.p.m. and devices built without further purification have electrical properties corresponding to  $10^{16}$  to  $10^{17}$  impurities/ $\text{cm}^3$ . Usually, before LPE growth, the experimentalists bake the whole device (In baths and InP substrates) and the final result is a decreasing impurity content towards about  $10^{15}$  impurities/ $\text{cm}^3$ . Two basic chemical problems are intermixed to obtain silicon low concentrations. First, what kind of purification is occurring before growth in the LPE reactors ? Second, is the reactor conception a limiting factor to the purification, by introducing a constant and low silicon equilibrium concentration in the InP/InGaAsP devices ? These two aspects are probably competitive in the LPE growth reactors, quite contrary to the lone purification process that seems to occur in GaAs growth reactors (1).

The impurity concentrations are so low that more often the chemical analysis is not possible and the electrical properties must be correlated to the elaboration process to guess what is the main electrically active impurity. Another solution is

to use thermodynamic calculations to investigate what are the gaseous species responsible of the transport processes and estimate their vapor pressures to quantify the purification limit which is theoretically possible to reach. These computer calculations are able to evidence very low concentrations because there is no theoretical limits. These calculations suppose the gaseous species are known and the thermodynamics of all the possible condensed phases well established.

## 2. CONDENSED PHASES AND GASEOUS SPECIES WHICH ARE KNOWN

The epitaxy furnace's materials which are maintained at high temperature during either the epitaxy growth or the baking time, are generally silica for the tube and graphite for the boat. The furnace atmosphere is  $H_2$  (Pressure = 1 Atm.)

and sometimes mixtures  $H_2$  + neutral gas or vacuum. If epitaxy temperatures are close to  $600^\circ C$ , the outgasing may be done at higher temperatures, up to  $800$  or  $900^\circ C$ . The condensed phases and the gaseous species that may exist in the high temperature zone come from the complex chemical system In - Si - P - C - O - H. The excess of  $SiO_2$ , graphite, In and InP phases involves thermodynamic forces that are constraining the whole set of gaseous chemical equilibria.

### 2.1. the known condensed phases.

The condensed phases come from the furnace materials,  $SiO_2$  and C (graphite), from the load, In and InP and also from the possible formation of other condensed phases like SiP, SiC, Si and  $In_2O_3$  combining the chemical constituents of the liquid epitaxy reactors. Because the equilibrium In (sat. with P)  $\rightleftharpoons$  InP(solid) is a necessary condition for the growth, P (red) cannot be formed in the furnace. The thermochemical datas come from (2), (3) and (4), while those for InP and SiP have been estimated (Annexe I). The  $In_2O_3$  phase which has already been studied by us (5) is quite similar to the proposed value (4).

When calculating the complex equilibrium, we assume the condensed phases are not miscible (their activities are = 1). This assumption is correct in this low temperature range. Thermochemical information are presented in Table I.

### 2.2. The known gaseous molecules.

The gaseous molecules in the In - Si - P - C - O - H chemical system are numerous and so we will eliminate the hydrocarbons to avoid some unusefull calculations. The calculations were performed only with the  $CH_4$ ,  $C_2H_4$  molecules. The low partial pressures of  $C_2H_4$  and  $C_2H_2$  show *a posteriori* that higher hydrocarbons are not important.

Thermodynamic datas for the gaseous species come from JANAF tables (2) or from original measurements as presented in Table I and annexe II.

## 3. THE EPITAXY REACTOR AS A CHEMICAL EQUILIBRIUM SYSTEM.

The  $H_2$  flow (1 Atm.) rate is usually very small, the gas residence time in the hot zone being about 1/2 to 1 minute. The time which is necessary to react between two gaseous species being about  $10^{-6}$  to  $10^{-5}$ s, we assume the chemical equilibrium is reached between the gaseous species. This cannot be assumed for silica and graphite reactions with gaseous species, but we know that a kinetic effect will decrease the Si and C based molecules concentrations ( $SiO$ ,  $SiH_4$ ,  $SiP_2$ ,  $CH_4$ , CO)

in the furnace. The same phenomenon occurs if, according to a large isothermal zone in these furnace, any diffusion process limits the mixing in the gaseous phase.

Our calculations, in the equilibrium state, represent always the maximal concentrations for the gaseous molecules that we can encounter in a LPE reactor (6).

TABLE I : thermodynamic datas for the complex equilibrium calculation of the LPE growth reactor

Phases	$-(G_T^{\circ}-H_{298}^{\circ})/T$ (cal. K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H_{f,298}^{\circ}$ (cal.mol <sup>-1</sup> )	Références
In (liquid)	13.820	0	3
Si (solid)	4.498	0	2
C	1.359	0	2
SiC	3.940	-17100	2
In <sub>2</sub> O <sub>3</sub>	25.800	-221300	4
InP	15.000	-13500	Annexe I
SiP	8.320	- 8077	//
SiO <sub>2</sub> (quartz)	9.910	-217700	2
In <sub>2</sub> (gas)	41.507	58000	3
P	38.980	79795	2
P <sub>2</sub>	52.110	42680	2
P <sub>4</sub>	66.893	30771	2
CP	51.661	128200	2 Annexe II
O <sub>2</sub>	49.005	0	2
PO	53.218	-2900	2
PO <sub>2</sub>	60.450	-63560	2
SiO	50.542	-24000	2
CO	47.217	-26417	2
CO <sub>2</sub>	51.072	-94051	2
H <sub>2</sub>	31.207	0	2
PH	46.900	60600	2
PH <sub>2</sub>	50.800	30100	2
PH <sub>3</sub>	50.238	5470	2
SiH	47.306	90000	2
SiH <sub>4</sub>	48.789	7800	2
CH <sub>4</sub>	44.490	-17895	2
C <sub>2</sub> H <sub>2</sub>	48.004	54190	2
C <sub>2</sub> H <sub>4</sub>	52.396	12540	2
CHP	51.375	36250	2
H <sub>2</sub> O	45.106	-57795	2
SiP	55.502	100260	Annexe II
SiP <sub>2</sub>	64.320	104120	
Si <sub>2</sub> P	65.465	74550	
CPSi	62.212	120600	
P <sub>2</sub> Si <sub>2</sub>	76.316	110330	
C <sub>2</sub> P	57.857	152200	
CPSi <sub>2</sub>	71.298	122876	
CP <sub>2</sub>	63.052	96100	
C <sub>2</sub> P <sub>2</sub>	66.327	103230	

Theoretically, the equilibrium state would be reached when stopping the  $H_2$  flow, but practically this equilibrium can be achieved with low flow rate of  $H_2$ .

### 3.1. $SiO_2 + \text{graphite} + H_2$ gas with In + InP load.

The equilibrium compositions are deduced by minimisation of the free energy of the whole chemical system (7). This minimisation is done with a  $SiO_2, C$  (graphite)

In and InP excess and with the initial pressure equal to 1 Atm. The whole pressure of the reacting system is maintained at 1 Atm. The calculation accuracy is fixed *a priori* at  $10^{-10}$  or  $10^{-11}$  moles (compared to 5 moles of  $H_2$  or  $SiO_2$ ....) and corresponds to a concentration threshold above which any condensed phase or gaseous molecule is participating to the calculation. So, when some gaseous species disappears in our calculations, it means its concentration is, at equilibrium, lower than our accuracy limit. For the condensed phases this means they don't exist.

The results are presented on the figure 1 in the temperature range 900 - 1100 K. In the gaseous phase, the silicon based molecules ( $SiH_4, SiO, SiP_2$ ) exist

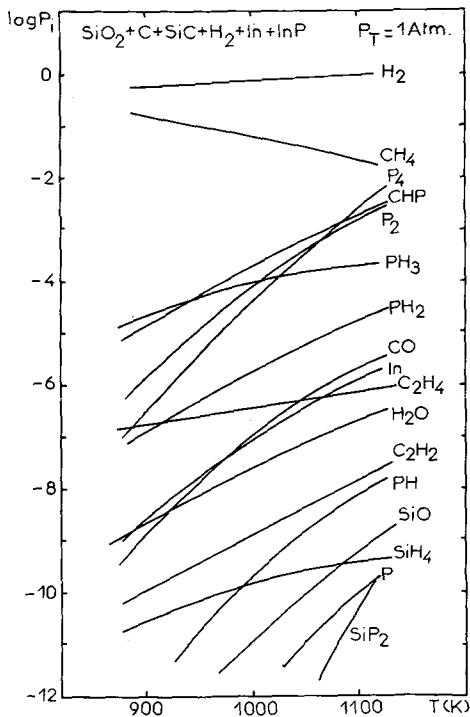


Fig. 1 : equilibrium partial pressures of gaseous species in a LPE growth reactor containing  $SiO_2$  (tube), C (graphite boat), In and InP as initial condensed phases in excess. The total pressure is 1 Atm. and the initial gas flow is pure hydrogen and the SiC phase is formed.

with a very low concentration. We also observe the formation of the SiC solid phase. As we know the SiC usually coats the dense graphite, the production of a certain quantity of this carbide can eliminate the contact of the graphite phase with our chemical system. The silicon activity must move upwards and a new calculation is necessary.

### 3.2. $SiO_2 + SiC + H_2$ gas with In + InP load.

Results are presented on figure 2. As we observed, the formation of pure Si phase shifts the complex chemical system towards an extreme limit where the activity of silicon is unit (its maximum value). In the epitaxy reactor the true working con-

dition of our system is probably between the chemical limits as defined by 3.1. and 3.2. cases. In the last one, the silicon based molecules concentration (mainly  $\text{SiH}_4$ ) is very important and the pollution of In + InP baths would occur instantaneously.

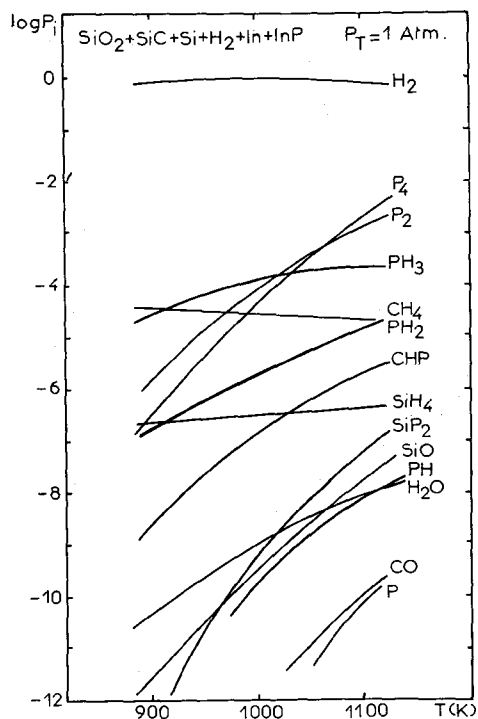


Fig. 2 : equilibrium partial pressures of gaseous species in a LPE growth reactor when the SiC condensed phase coats entirely the graphite boat. In this case, the pure silicon phase is formed and the pressures of silicon based gaseous species increase drastically as compared to Fig. 1.

### 3.3. Controlling the phosphorus pressure through $\text{PH}_3$ (Phosphine) additions.

As shown by the results, the phosphorus equilibrium pressure above the In - InP two phases system is established mainly through the  $\text{P}_2$ ,  $\text{P}_4$ ,  $\text{PH}_3$ ,  $\text{PH}_2$ ,  $\text{PH}$ ,  $\text{CHP}$  and  $\text{SiP}_2$  molecules. The partial pressures of  $\text{P}_2$ ,  $\text{P}_4$  and In are imposed by the In  $\rightleftharpoons$  InP equilibrium, since  $\text{PH}_3$ ,  $\text{PH}_2$ ,  $\text{PH}$  partial pressures are imposed by this equilibrium and the  $\text{H}_2$  pressure (quite equal to the total pressure). The CHP molecule is very important when the graphite boat is not coated with SiC (fig. 1), but becomes negligible when this carbide coats the boats.

When working under  $\text{H}_2$  flow in the furnace, all these species consume the phosphorus included in the InP substrates and explain that some experimentalist tried to counteract this process by introducing  $\text{PH}_3$  in the  $\text{H}_2$  flow. This introduction must be done taking into account the  $\text{PH}_3$  decomposition and reaction with the furnace's materials as shown on fig. 3 and Table II. To avoid the attack of the InP

substrates, the  $\text{PH}_3$  concentration in  $\text{H}_2$  flow must be sufficient : on fig. 3, the equilibrium pressures of  $\text{PH}_3$  in the furnace are compared to the introduction pressures in the  $\text{H}_2$  flow, for a graphite boat and a SiC coated boat (as the total pressure is 1 Atm., the partial pressures are the molar concentrations). The threshold concentrations as experimentally determined (8) to (11) to avoid substrates degradation agree with our thermodynamic calculations. Moreover, the Clawson and Coll. (10) (11) values agree with us, but their interpretation with an hypothetic  $\text{PH}_3$  decomposition kinetic low rate below  $710^\circ\text{C}$  cannot be confirm and probably comes from their thermodynamic data's choice.

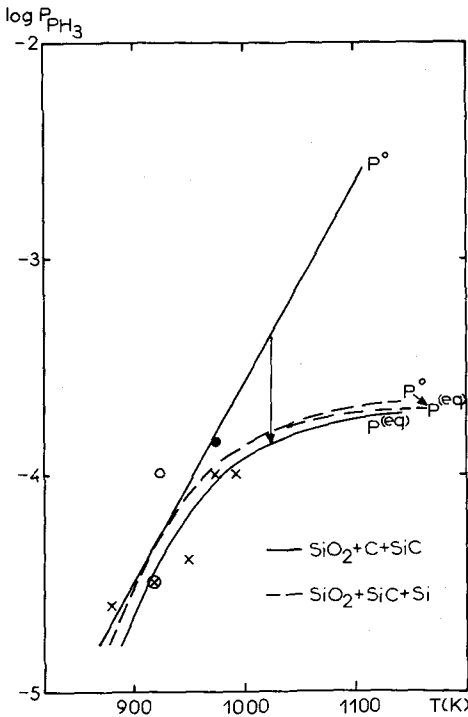
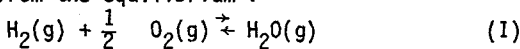


Fig. 3 : equilibrium pressures of phosphine ( $P^{\text{eq}}$ ) and initial pressures of  $\text{PH}_3$  ( $P^\circ$ ) which is necessary to introduce in view of counteracting the thermal dissociation and reaction of  $\text{PH}_3$  with the furnace materials. Experimental thresholds for InP degradation : x Ref. 10, o Ref. 11, O Ref. 9 and Ref. 8.

A general result for the two previous cases C excess or SiC excess, is we never observed some  $\text{SiP}$  or  $\text{In}_2\text{O}_3$  solid phases formation. This can be explained by the In + InP excess and the very low oxygen potential in the furnace as we have calculated from the equilibrium :



$$10^{-44} < P(\text{O}_2) < 10^{-34} \text{ with SiC + Si excess}$$

$$\text{and } 10^{-40} < P(\text{O}_2) < 10^{-31} \text{ with C + SiC excess.}$$

**TABLE II** : Equilibrium concentrations of  $\text{PH}_3$  in the reactor and initial concentrations which are necessary to counteract the substrates degradation. (Total pressure = 1 Atm.)

Reactor with C excess			
T (K)	$\frac{\text{PH}_3}{\text{PH}_3 + \text{PH}_2 + \text{PH} + \text{HCP}}$	$P_{\text{PH}_3 \text{ equil.}}$ (Atm)	$P_{\text{PH}_3 \text{ to introduce}}$
900	65	$3,2 \cdot 10^{-5}$	$4,9 \cdot 10^{-5}$
1000	26	$1,1 \cdot 10^{-4}$	$4,1 \cdot 10^{-4}$
1100	8	$2,5 \cdot 10^{-4}$	$3,1 \cdot 10^{-3}$
Reactor with an excess of SiC			
900	99	$4,5 \cdot 10^{-5}$	$4,5 \cdot 10^{-5}$
1000	98	$1,2 \cdot 10^{-4}$	$1,2 \cdot 10^{-4}$
1100	92	$2,6 \cdot 10^{-4}$	$2,8 \cdot 10^{-4}$

#### 4. HYDROGEN PRESSURE INCIDENCE ON THE SILICON TRANSPORT PROCESS

In part 3, we have observed that the silicon is mainly transported through the  $\text{SiH}_4$  molecule and with lower efficiency through  $\text{SiO}$  and  $\text{SiP}_2$  molecules. As the  $\text{SiH}_4$  pressure is directly bounded to the  $\text{H}_2$  pressure, the influence of the  $\text{H}_2$  decreasing pressure has been studied. Practically, this condition can be realised with  $\text{H}_2$  and rare gas mixtures at a 1 Atm. total pressure. As in part 3, we calculated for the two chemical system :  $\text{SiC} + \text{C}$  or  $\text{SiC} + \text{Si}$ .

##### 4.1. Furnace with C excess.

The results show that the  $\text{SiC}$  formation occurs, but its amount decreases with the  $\text{H}_2$  pressure and so we suppose the coating of the boat cannot be done completely. We also calculated the limit which is the absolute vacuum (Table III). In fact, even if there is no contact between the silica tube and the graphite boat, the residual gases ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ....) initiate the exchange reaction and the  $\text{SiC}$  formation is quite possible.



As the  $H_2$  pressure decreases, all the gaseous species containing H have their pressures decreasing as shown on the figures 4 and 5 :

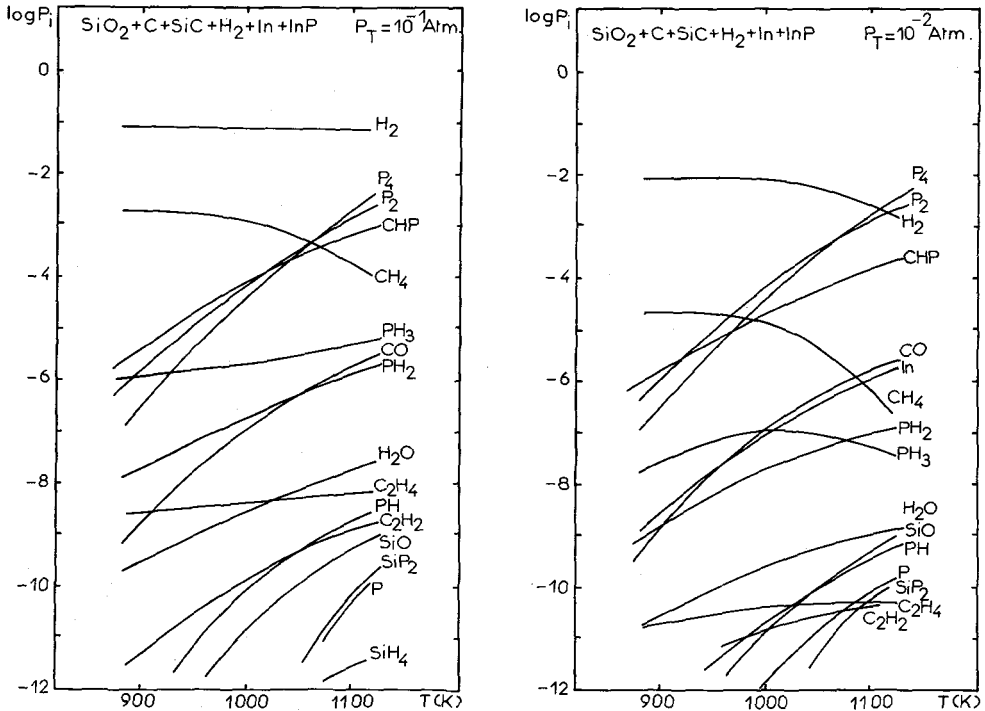
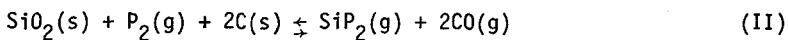


Fig. 4 and 5 : influence of decreasing total  $H_2$  input pressure (as compared to Fig.1) on the equilibrium partial pressures in the LPE furnace when graphite (boat) and SiC partial coating exist all together.

The  $SiH_4$  pressure becomes lower than the  $SiO$  pressure at 900 K and  $P(H_2) < 10^{-1}$  Atm. All the gaseous species which are lower than the accuracy limit of the calculations are calculated through the equilibria :



The oxygen partial pressures are calculated through :



T A B L E III : partial pressures of gaseous species in a LPE reactor under vacuum and condensed phases which exist .			
Gaseous Species	Reactor with C excess : $\text{SiO}_2 + \text{C} + \text{SiC}^{(1)} + \text{In} + \text{InP}$		
	Partial Pressures (Atm.)		
	T = 900 K	1 000 K	1 100 K
In	$4.04 \cdot 10^{-9}$	$9.44 \cdot 10^{-8}$	$1.24 \cdot 10^{-6}$
P <sub>2</sub>	$1.71 \cdot 10^{-6}$	$8.64 \cdot 10^{-5}$	$2.12 \cdot 10^{-3}$
P <sub>4</sub>	$5.01 \cdot 10^{-7}$	$6.42 \cdot 10^{-5}$	$3.34 \cdot 10^{-3}$
P	-	-	$9.5 \cdot 10^{-11}$
SiO	$7.00 \cdot 10^{-14}$	$1.14 \cdot 10^{-11}$	$7.4 \cdot 10^{-10}$
SiP <sub>2</sub>	$5.04 \cdot 10^{-16}$	$3.77 \cdot 10^{-13}$	$8.7 \cdot 10^{-11}$
CO	$1.87 \cdot 10^{-9}$	$1.11 \cdot 10^{-7}$	$3.09 \cdot 10^{-6}$
O <sub>2</sub> *	$2.13 \cdot 10^{-40}$	$1.49 \cdot 10^{-35}$	$1.34 \cdot 10^{-31}$
O *	$7.79 \cdot 10^{-32}$	$6.01 \cdot 10^{-28}$	$9.07 \cdot 10^{-25}$
Reactor with an excess of SiC : $\text{SiO}_2 + \text{SiC} + \text{Si}^{(1)} + \text{In} + \text{InP}$			
In	ib. excess C	ib. excess C	ib. excess C
P <sub>2</sub>	ib "	ib "	ib "
P <sub>4</sub>	ib "	ib "	ib "
P	ib "	ib "	ib "
SiO	$5.19 \cdot 10^{-12}$	$5.19 \cdot 10^{-10}$	$2.32 \cdot 10^{-8}$
SiP <sub>2</sub>	$2.75 \cdot 10^{-12}$	$7.68 \cdot 10^{-10}$	$8.09 \cdot 10^{-8}$
CO	$1.35 \cdot 10^{-15}$	$1.67 \cdot 10^{-14}$	$1.19 \cdot 10^{-13}$
O <sub>2</sub> *	$1.01 \cdot 10^{-85}$	$5.1 \cdot 10^{-78}$	$9.68 \cdot 10^{-72}$
O *	$1.69 \cdot 10^{-54}$	$3.51 \cdot 10^{-49}$	$7.70 \cdot 10^{-45}$
(1) SiC and Si are the phases which are formed.			
* These pressures are calculated from P <sub>CO</sub> and the equilibria II, III, IV and V			

#### 4.2 : Silicon carbide coated boat.

As in part 3, when SiC coats the graphite boat, the pure Si solid phase appears and the silicon activity is at its maximal value ( $a = 1$ ), the chemical system being SiC + Si. Evidently, the gaseous species with the Si atom have their

pressures increasing (fig. 6 and 7). At 900 K, the  $\text{SiH}_4$  molecule remains the more volatil molecule when  $P(\text{H}_2) > 10^{-2}$  Atm. Under vacuum,  $\text{SiH}_4$  disappears and  $\text{SiO}$  and  $\text{SiP}_2$  are the transporting species (table III). This transport process is the one which has been observed (13) when outgasing at high temperature (1100-1200 K), and analysing the silicon included in the In + InP baths. As shown in table III, the calculated oxygen pressures are very low, corresponding to free silicon in the furnace. This is not realistic because leaks, diffusion through silica or gasket's outgasing must occur even with a very low rate. So the  $\text{SiO}$  and  $\text{SiP}_2$  pressures have their maximal value but probably never attained.

As a conclusion the lone advantage for working with reduced  $\text{H}_2$  pressure is the decreasing  $\text{PH}_3$ ,  $\text{PH}_2$ ,  $\text{PH}$  and  $\text{CHP}$  partial pressures and consequently less degradation of the substrates.

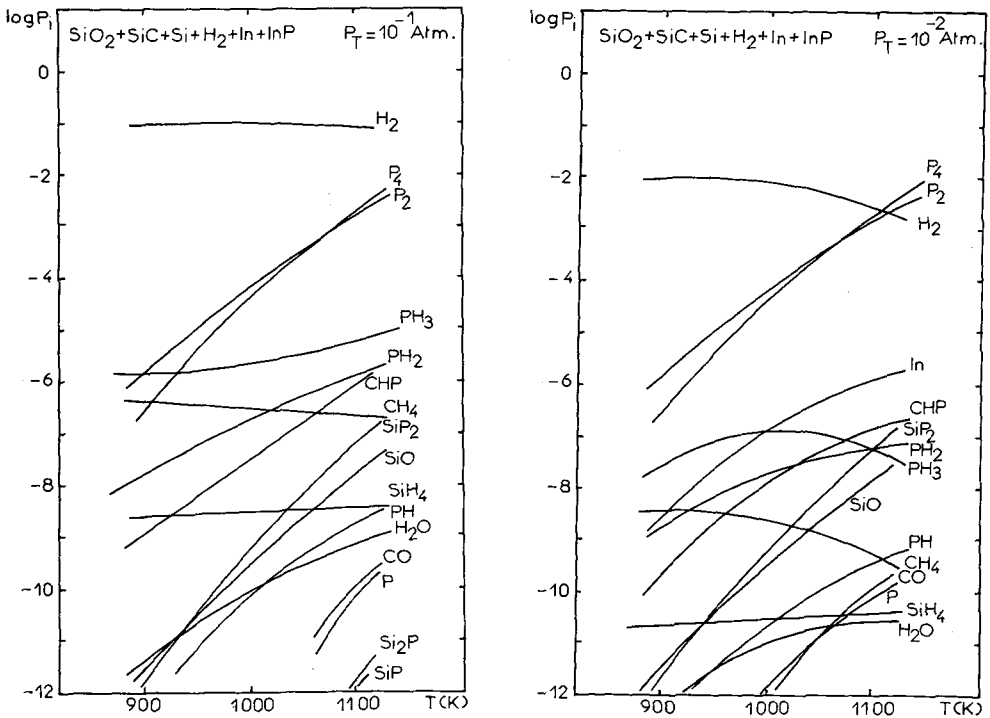
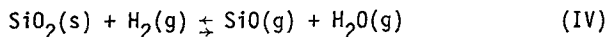


Fig. 6 and 7 : influence of decreasing total  $\text{H}_2$  input pressure (as compared to Fig.2) on the partial pressures in the LPE furnace when SiC coats the graphite boat.

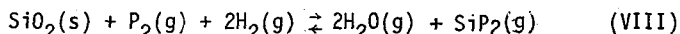
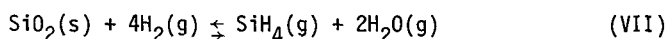
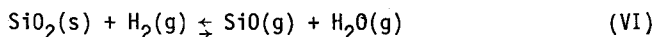
5. ADDING WATER IN  $\text{H}_2$  FLOW

Several experimentalists (8)(12)(13) introduced some water in the  $\text{H}_2$  flow to move the equilibrium reaction :



towards reduced  $\text{SiO}(\text{g})$  pressure. Eastman and Coll. (14) proposed a theoretical limit ( $4 \cdot 10^{14}$  impurities/ $\text{cm}^3$ ), based on the activity coefficient of Si at infinite dilution in Indium calculated by Thurmond (15). As the water vapor pressures which are introduced are generally higher than those calculated at equilibrium with pure  $\text{H}_2$  flow, we have to recalculate the new equilibrium state which is imposed by initial water

concentration in the  $H_2$  flow. On the figures 8 to 11, the results are such than the SiC phase disappears and the  $SiH_4$ , SiO and  $SiP_2$  gaseous species decrease when the water content increases. In table IV the theoretical values for these species are calculated through the equilibria :



where the main gaseous species pressures are known by the complex equilibrium calculation. The CO,  $O_2$  and O pressures are deduced from the equilibria I, IV, V and :



The decreasing partial pressures of silicon gaseous species is due to the lowering silicon activity in silica when increasing water content in the  $H_2$  flow, as shown in fig. 12. As a consequence the SiC phase is no longer existing.

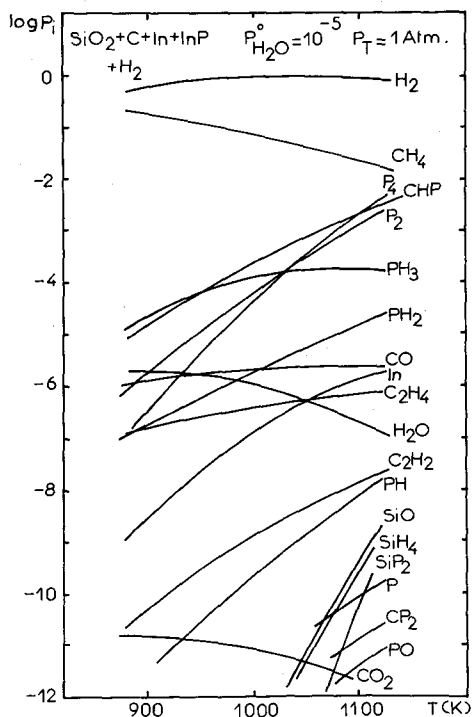
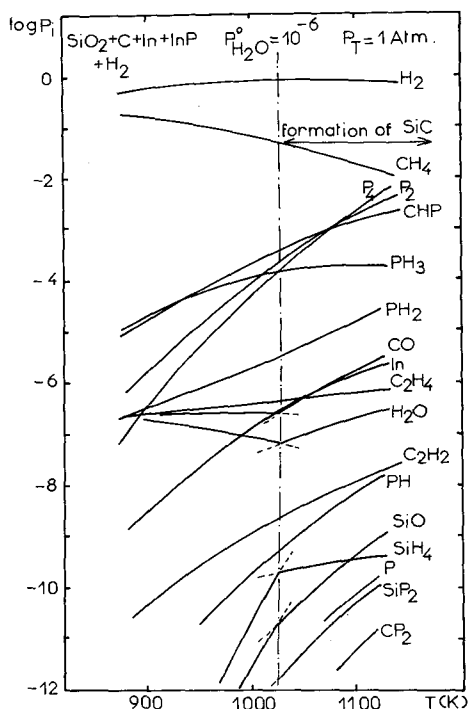


Fig. 8 to 11 : influence on the equilibrium partial pressures of the water content in  $H_2$  flow. The SiC condensed phase disappears and the silicon based gaseous species partial pressures decrease.

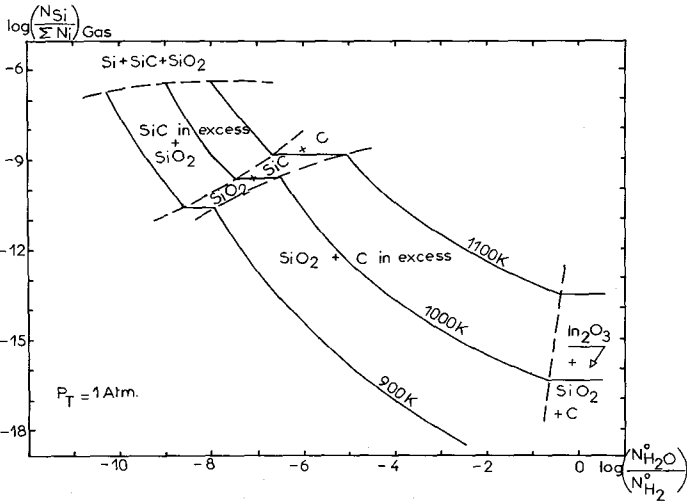
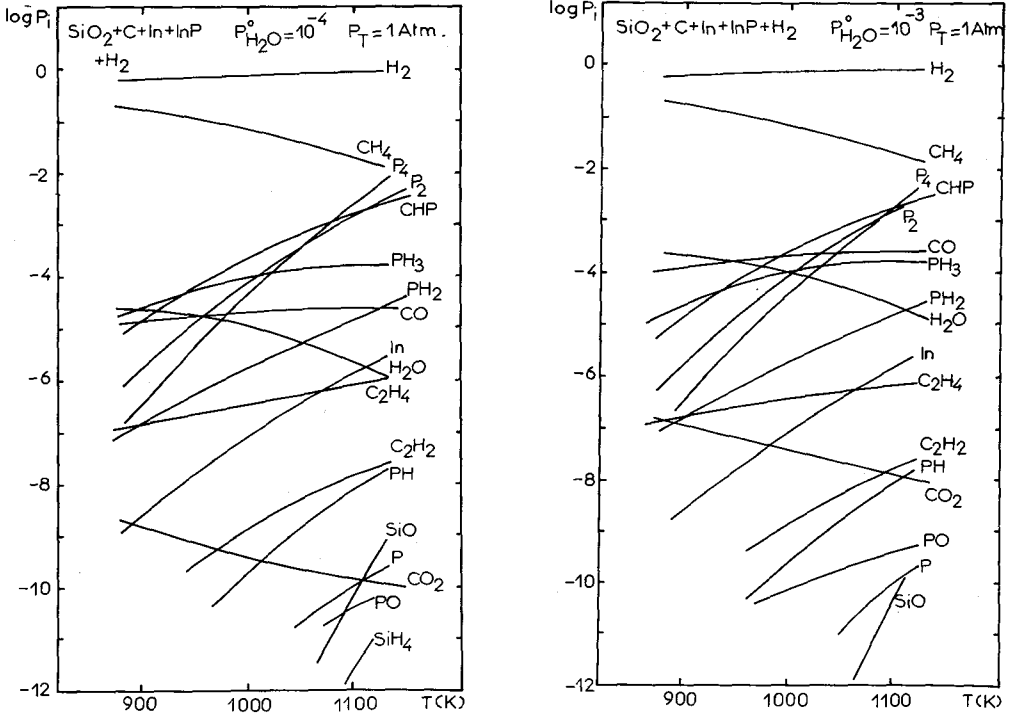


Fig. 12 : logarithms of the molar fraction of Si in the gaseous phase as a function of initial water content in  $H_2$  flow. The domains of existence are represented for the different condensed phases.

**T A B L E IV** : partial pressures of gaseous species with oxygen or/and silicon as a function of initial water content in  $H_2$  flow ( $P_T = 1$  atm.). The pressures lower than  $10^{-11}$  atm. are calculated through the equilibrium constants of known reactions

T(K)	Gaseous Species	Water content in $H_2$ flow : $H_2O/H_2$			
		partial pressures (Atm.)			
		$10^{-6}$	$10^{-5}$	$10^{-4}$	$10^{-3}$
900	$H_2$	0.796	0.796	0.796	0.795
	SiO	$8 \cdot 10^{-16}$	$8 \cdot 10^{-17}$	$8 \cdot 10^{-18}$	$8 \cdot 10^{-19}$
	SiH <sub>4</sub>	$5.9 \cdot 10^{-15}$	$6 \cdot 10^{-17}$	$6 \cdot 10^{-19}$	$5.9 \cdot 10^{-21}$
	SiP <sub>2</sub>	$6.7 \cdot 10^{-20}$	$6.7 \cdot 10^{-22}$	$6.6 \cdot 10^{-24}$	$6.7 \cdot 10^{-26}$
	CO	$1.6 \cdot 10^{-7}$	$1.6 \cdot 10^{-6}$	$1.6 \cdot 10^{-5}$	$1.6 \cdot 10^{-4}$
	CO <sub>2</sub>	$1.5 \cdot 10^{-13}$	$1.5 \cdot 10^{-11}$	$1.5 \cdot 10^{-9}$	$1.5 \cdot 10^{-7}$
	H <sub>2</sub> O	$3.2 \cdot 10^{-7}$	$3.2 \cdot 10^{-6}$	$3.2 \cdot 10^{-5}$	$3.3 \cdot 10^{-4}$
	O <sub>2</sub>	$1.6 \cdot 10^{-36}$	$1.6 \cdot 10^{-34}$	$1.6 \cdot 10^{-32}$	$1.6 \cdot 10^{-30}$
	O	$6.8 \cdot 10^{-30}$	$6.8 \cdot 10^{-29}$	$6.8 \cdot 10^{-28}$	$6.8 \cdot 10^{-27}$
1 000	$H_2$	0.917	0.917	0.917	0.917
	SiO	$4 \cdot 10^{-12}$	$4 \cdot 10^{-13}$	$4 \cdot 10^{-14}$	$4 \cdot 10^{-15}$
	SiH <sub>4</sub>	$2.5 \cdot 10^{-11}$	$2.5 \cdot 10^{-13}$	$2.5 \cdot 10^{-15}$	$2.5 \cdot 10^{-17}$
	SiP <sub>2</sub>	$4.6 \cdot 10^{-14}$	$4.6 \cdot 10^{-16}$	$4.6 \cdot 10^{-18}$	$4.6 \cdot 10^{-20}$
	CO	$3.2 \cdot 10^{-7}$	$3.2 \cdot 10^{-6}$	$3.2 \cdot 10^{-5}$	$3.2 \cdot 10^{-4}$
	CO <sub>2</sub>	$5.8 \cdot 10^{-14}$	$5.8 \cdot 10^{-12}$	$5.8 \cdot 10^{-10}$	$5.8 \cdot 10^{-8}$
	H <sub>2</sub> O	$1.2 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$
	O <sub>2</sub>	$1.2 \cdot 10^{-34}$	$1.2 \cdot 10^{-32}$	$1.2 \cdot 10^{-30}$	$1.2 \cdot 10^{-28}$
	O	$1.7 \cdot 10^{-27}$	$1.7 \cdot 10^{-26}$	$1.7 \cdot 10^{-25}$	$1.7 \cdot 10^{-24}$
1100	$H_2$	0.958	0.958	0.958	0.958
	SiO	$7.4 \cdot 10^{-10}$	$6 \cdot 10^{-10}$	$6 \cdot 10^{-11}$	$6.1 \cdot 10^{-12}$
	SiH <sub>4</sub>	$6 \cdot 10^{-10}$	$4 \cdot 10^{-10}$	$4 \cdot 10^{-12}$	$3.9 \cdot 10^{-14}$
	SiP <sub>2</sub>	$8.5 \cdot 10^{-11}$	$5.6 \cdot 10^{-11}$	$5.6 \cdot 10^{-13}$	$5.7 \cdot 10^{-15}$
	CO	$3.1 \cdot 10^{-6}$	$3.8 \cdot 10^{-6}$	$3.8 \cdot 10^{-5}$	$3.8 \cdot 10^{-4}$
	CO <sub>2</sub>	$8.5 \cdot 10^{-13}$	$1.3 \cdot 10^{-12}$	$1.2 \cdot 10^{-10}$	$1.3 \cdot 10^{-8}$
	H <sub>2</sub> O	$2.7 \cdot 10^{-7}$	$3.3 \cdot 10^{-7}$	$3.3 \cdot 10^{-6}$	$3.3 \cdot 10^{-5}$
	O <sub>2</sub>	$1.3 \cdot 10^{-31}$	$2.0 \cdot 10^{-31}$	$2.0 \cdot 10^{-29}$	$2.0 \cdot 10^{-27}$
	O	$9 \cdot 10^{-25}$	$1.1 \cdot 10^{-24}$	$1.1 \cdot 10^{-23}$	$1.1 \cdot 10^{-22}$

6 - ESTIMATED SI POLLUTION OF THE InP SUBSTRATES AND In BATHS

The calculation of the Si concentration in the liquid In saturated with phosphorus (In + InP coexisting phases), or the Si contamination of InP substrates can be fully performed if the thermodynamic properties for Si and P dilute solutions in In are known. As these values are not available, the calculations are done from the In-Si binary system.

The infinite dilution activity coefficient,  $\gamma^{\infty}_{Si(In)}$ , of silicon in Indium is estimated from the Si-In phase diagram assuming the liquid solution is pseudo-regular (15)(16)(17), i-e the  $\alpha = a-bT$  coefficient is varying with the temperature. From the  $a$  coefficient, the  $\gamma^{\infty}_{Si}$  is deduced :

$$a = \Delta H^{\infty}_{Si(In)} = RT \ln \gamma^{\infty}_{Si(l)}$$

The assumption of a pseudoregular solution has been checked successfully by calorimetric measurements (18) of the partial enthalpy of Si in In at infinite dilution  $\Delta H^{\infty}_{Si(In)}$ . The activity coefficient of Si in the solid InP phase is deduced from the  $\gamma^{\infty}_{Si(In)}$  and the distribution coefficient (19)

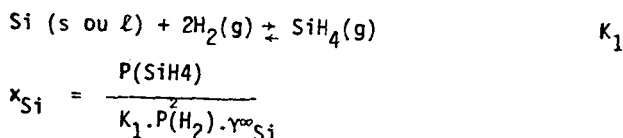
$$k = \frac{x_{Si}(\text{in InP})}{x_{Si}(\text{in In sat. with InP})} \sim 4$$

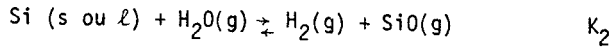
$\Delta H_m(Si) = 12\ 000\ \text{cal}\cdot\text{mol}^{-1}$  (2) melting enthalpy of Si,  $T_m(Si) = 1685\ \text{K}$  (2) melting temperature of Si. We deduce the activity coefficient of silicon in solid InP (Table V)

T A B L E V : calculated values of the silicon infinite dilution activity coefficient in liquid indium or in solid InP substrates.

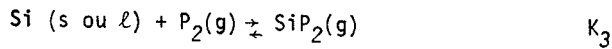
T(K)	$\gamma^{\infty}_{Si}(\text{in In liq.})$	$\gamma^{\infty}_{Si}(\text{in solid InP})$
900	110	627
1 000	58	168
1 100	34	58

The silicon concentration in the liquid In bath saturated with InP or the InP substrates are calculated through any equilibrium reactions because the silicon activity has a unic value in the liquid epitaxy reactor :





$$x_{\text{Si}} = \frac{P(\text{SiO}) \cdot P(\text{H}_2)}{K_2 \cdot P(\text{H}_2\text{O}) \cdot \gamma_{\text{Si}}^{\infty}}$$



$$x_{\text{Si}} = \frac{P(\text{SiP}_2)}{K_3 \cdot P(\text{P}_2) \cdot \gamma_{\text{Si}}^{\infty}}$$

The estimated Si concentration in InP is presented on the Fig. 13 and table VI for different chemical environments. On Fig. 13, we also quoted the concentrations which are reported by authors (12)(13) before and after baking or water additions. The agreement between these results and our calculations proves the true chemical behavior of the LPE reactor is close to  $\text{SiO}_2 + \text{C excess} + \text{SiC}$  without  $\text{H}_2\text{O}$  vapor, and close to  $\text{SiO}_2 + \text{C excess}$  when adding water in the  $\text{H}_2$  flow.

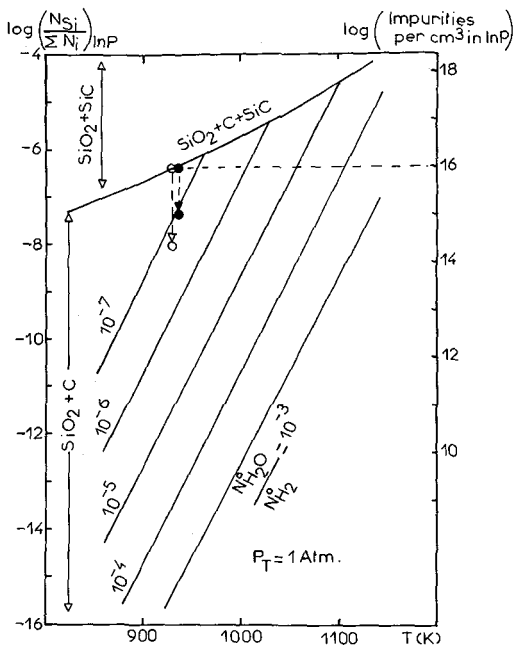


Fig. 13 : logarithms of the molar fraction of silicon in InP substrates as a function of water content in  $\text{H}_2$  flow. Experimental determinations :  $\circ$  Ref. (12),  $\bullet$  Ref. (13). Upper values are without baking, lower values after baking with  $\text{H}_2\text{O}$  in  $\text{H}_2$  flow.



T A B L E VI

Silicon molar fraction at equilibrium for InP substrates as a function of the chemical environment in the LPE reactor :  $\text{SiO}_2$  tube + graphite boat +  $\text{H}_2$  (chemical system  $\text{SiC} + \text{C} + \text{H}_2$ ) or with  $\text{SiC}$  coating ( $\text{SiC} + \text{Si} + \text{H}_2$ ) or vacuum, and with water content in the  $\text{H}_2$  flow. Total pressure = 1 Atm.

molar fraction $x_{\text{Si}}$	Reactor with $\text{SiC} + \text{Si} + \text{H}_2$	Reactor with $\text{SiC} + \text{C} + \text{H}_2$	Reactor under vacuum	Water input: $N(\text{H}_2\text{O})/N(\text{H}_2)$			
				$10^{-6}$	$10^{-5}$	$10^{-4}$	$10^{-3}$
900 K	$1.2 \cdot 10^{-3}$	$2.7 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$3.3 \cdot 10^{-11}$	$3.3 \cdot 10^{-13}$	$3.3 \cdot 10^{-15}$	$3.3 \cdot 10^{-17}$
1 000 K	$8.5 \cdot 10^{-3}$	$4.2 \cdot 10^{-6}$	$4.2 \cdot 10^{-6}$	$5.1 \cdot 10^{-7}$	$5.1 \cdot 10^{-9}$	$5.1 \cdot 10^{-11}$	$5.1 \cdot 10^{-13}$
1 100 K	$4.4 \cdot 10^{-2}$	$4.4 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-7}$	$3.0 \cdot 10^{-9}$

## 7 - CONCLUSION

The origin of the Si pollution of InP substrates semi-conductor devices growth by LPE, is either the initial silicon composition of In or the attack of furnace's quartz tubes. The transport of Si is done through the  $\text{SiH}_4$ , SiO and

$\text{SiP}_2$  gaseous species in conventional devices with pure  $\text{H}_2$  flow. When using graphite boats the SiC solid phase is formed. In a conventional device, the silicon activity is fixed by the complex chemical system  $\text{SiO}_2 + \text{C} + \text{SiC}$  and the contamination of the

InP substrates is about  $10^{16}$  impurities per  $\text{cm}^3$ , this last value being in agreement with experimental datas ( $t = 640^\circ\text{C}$ ).

The addition of water in  $\text{H}_2$  flow enhances a decreasing silicon contamination in the reactor. The SiC phase is no longer formed and the Si impurity concentration decreases. Then the  $\text{SiH}_4$ , SiO and  $\text{SiP}_2$  partial pressures are so low than the silicon

content of Indium bath or InP substrate produces this species and a purification process starts during the baking time. There is no theoretical limits for this purification (in the desired range for electronic devices), although an experimental

limit has been reached :  $4 \cdot 10^{14}$  to  $10^{15}$  impurities/ $\text{cm}^3$ .

Either this limit corresponds to other impurities or to practical features like a too long baking time. Perhaps it would be more convenient to purify the pure In basic constituent independantly before InP substrate preparation and multilayers epitaxy growth from Indium baths.

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ANNEXE I : CONDENSED PHASES

I - The InP compound

- The  $C_p$  and  $H_T^\circ - H_{298}^\circ$  from Pankratz's measurements (a) between 394 and 1097 K.
- $S_{298}^\circ$  extrapolated to 0 K from Piesbergen's measurements (b) between 12 and 273 K.
- $\Delta H_f^\circ(\text{InP}, s, 298 \text{ K})$  : two groups of calorimetric measurements, one about 13-14 Kcal.mol.<sup>-1</sup>, the other around 17-18 Kcal.mol.<sup>-1</sup>, are discriminated by consistency with  $S_{298}^\circ$  and  $\Delta G_f^\circ(\text{InP}, 1000 \text{ K})$  obtained from  $P_2$  and  $P_4$  pressure measurements. The second and third law calculations of  $\Delta H_f^\circ$  from pressures measurements are consistent with the PRATT and COLL. (c) calorimetric determination. Our value is quite similar to the KNACKE and BARIN compilation (Réf. 4) as presented in table :

InP	$S_{298}^\circ$ Cal.K <sup>-1</sup> .mol. <sup>-1</sup>	$\Delta H_f^\circ 298$ Cal.mol. <sup>-1</sup> .
KNACKE and BARIN	14.280	-13830
Our values	15.00	-13500

$$- C_p = 12.27 - 0.114 \times 10^{-6} T^{-2} \quad 298 < T < 910 \text{ K}$$

Solid-solid transformation at  $T=910 \text{ K}$ ,  $\Delta H_T=90 \text{ cal}$ .

$$C_p = 5.89 + 0.64 \times 10^{-2} T \quad T > 910 \text{ K}.$$

2 - The SiP compound

- $C_p$  and  $H_T^\circ - H_{298}^\circ$  are estimated similar to InP from 298 to 1100 K because no experimental data are available.
- $S_{298}^\circ$  is from Goncharov and Coll. (d) measurements.
- $\Delta H_f^\circ 298$  has been estimated by Barin (Réf. 4) and Goncharov (d) respectively

-14800 and -10850 cal.mol<sup>-1</sup>. The reference is P red. We recalculated with the new S<sub>298</sub><sup>o</sup> value, our C<sub>p</sub> estimate and from the phase diagram (total phosphorus pressure = 1 Atm.)(e). In the table our value appears different from the others :

Si P	S <sub>298</sub> <sup>o</sup> Cal.K <sup>-1</sup> .mol <sup>-1</sup> .	ΔH <sub>f298</sub> <sup>o</sup> Cal.mol <sup>-1</sup> .
Barin and Knacke (4)	7.80	-14800
Goncharov and Coll. (d)	8.32	-10850
Our value	8.32	- 8077

- C<sub>p</sub> : the same as for InP

### 3 - References

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### ANNEXE II: GASEOUS SPECIES

These thermodynamic properties are established from original literature datas for the gaseous molecules which are not compiled in thermodynamic tables.

#### 1 - The systems Si-P and Si-C-P

From S. SMOES, D. DEPIERE, J. DROWART, Rev.Int.Hautes Temper. et Refract., 9, (1972), 171-176, the SiP, Si<sub>2</sub>P, SiP<sub>2</sub>, Si<sub>2</sub>P<sub>2</sub>, SiCP and SiPCSi molecules have been measured. The thermodynamic datas provide from partial pressure measurements by mass spectrometry. The molecular parameters are estimated to calculate the entropy. When various structures are available, we chose the most stable. So the pressure of this species in the reactor is maximal. The difference between the structures leads to 2 or 3 Kcal.mol<sup>-1</sup>. shift in ΔH<sub>f</sub><sup>o</sup>, and so the pressure may vary by a factor of 10.

(This is available only for complex molecules).

#### 2 - The C-P system

Two references: a - SMOES S., MYERS C.E., DROWART J., Chem.Phys. letters, 8, (1971), 10-12.

b - KORDIS J., GINGERICH K.A., J.Chem.Phys., 58, (1973), 5058-5066. where the CP, C<sub>2</sub>P, CP<sub>2</sub> and C<sub>2</sub>P<sub>2</sub> molecules are investigated. For the CP molecule, the structure is known (see JANAP tables) but its ΔH<sub>f</sub><sup>o</sup> is not accurately known (± 23 Kcal.mol<sup>-1</sup>). We chose the mean value for ΔH<sub>f</sub><sup>o</sup> coming from the two references a and b.