

Compatibility Relationship among Reaction Equilibria, Equivalence Principle of Reaction Approaches, and Silicon Contamination in Semiconductors

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This paper discovers some shortcomings in the algorithm for the incorporation of Si into GaAs in the GaAs VPE process. These faults arise from neglecting a link, the compatibility relationship, in chemical thermodynamics. The meaning of said relationship is as follows: In an equilibrium complex system, each species can only contribute one and the same quantity (its equilibrium quantity) to the different equilibria of the various reactions involving it; yet even under this restriction, every equilibrium constant is satisfied, and all the reaction equilibria coexist compatibly in the system. Only by adding the relationship can the equilibrium theory for the complex system be complete. This paper also tells its position in chemical thermodynamics. Such a compatibility concept directly leads to an equivalence principle: In a complex system, a certain species can usually be simultaneously formed by many chemical reactions; when the system has reached equilibrium under fixed environmental conditions, the equilibrium quantity of said species calculated according to each chemical equation of these reactions will be equal and the various reaction approaches will be equivalent, provided that for all the reactants and all the other products of these reactions their equilibrium quantities in the system are respectively taken as corresponding knowns for the calculations, which is extremely useful for seeking a functional relation among the species' equilibrium quantities in a system (Si contamination is one of the examples). Under the guidance of those arguments, the various schools' algorithms for the Si contamination can be uniformized and simplified, and the contamination quantity relation between Si and O, two very important impurities, is found.

Discovery of the Problem

In the studies of GaAs vapor-phase epitaxy using the Ga–AsCl₃–H₂ system, Cairns and Fairman¹ first observed a mole fraction effect: the carrier concentration in the epitaxial layer decreases with the increase of the mole fraction of AsCl₃ carried into the reaction tube by hydrogen. DoLorenzo and Moore,² following Knight et al.,³ performed a systematic study on it. At present, a publicly established theory for said mole fraction effect is as follows. The HCl formed by the action of H₂ on AsCl₃ reacts with the quartz reaction tube wall, forming various chlorosilanes such as SiCl₄, SiHCl₃, SiH₂Cl₂, and SiH₃Cl. They move onto the surface of the epilayer being grown and dissociate out silicon thereon. These dissociation reactions are inhibited by HCl, which exhibits said mole fraction effect, as shown in Figure 1.

Calculation of Si activity in the epilayer proceeds pursuant to a local equilibrium assumption. The assumption extensively used in the open flow system with different temperature distributions in the flowing direction, or as called, the local complete-equilibrium assumption, can be expressed by us as follows: While gas mixture steadily flows through the horizontal reaction tube at low speed (without turbulent or laminar flow, without the mixture's components diffusing in the flowing direction), its chemical reaction rates and thermal movement speeds of molecules are far faster than the flow speed, so that for the mixture, when flowing to each cross section vertical to the flowing direction, its temperature can reach equilibrium with the temperature of the cross section's environment, all its components can reach chemical equilibrium with each other, with the condensed substance species being contacted (quartz tube wall, Ga source, epilayer, etc.), and it can homogeneously

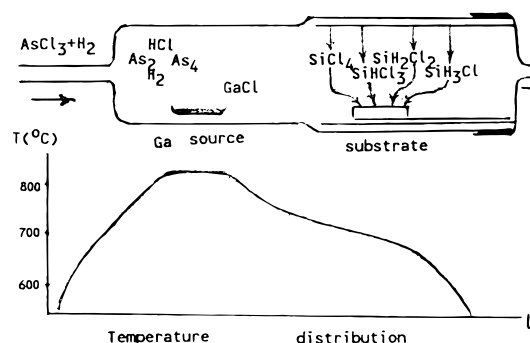


Figure 1. Schematic diagram of silicon contamination in the AsCl₃–Ga–H₂ system.

distribute in the whole isothermal cross section (without considering the height distributions of the different-weight molecules caused by the gravitational field).

The crux of this new problem lies in that several species containing Si all make contributions to Si contamination through their respective reactions. In 1971, the core of the algorithm created by the forerunners of scientists^{2,4} is that, in the vapor phase, the sum of the partial pressures (respectively designated as P') of the chlorosilanes formed in the tube wall reactions and in equilibrium with the tube wall is exactly equal to the sum of the partial pressures (respectively designated as P'') of the chlorosilanes in equilibrium with the Si activity in the epilayer. That is,

$$P'_{\text{SiCl}_4} + P'_{\text{SiHCl}_3} + P'_{\text{SiH}_2\text{Cl}_2} + P'_{\text{SiH}_3\text{Cl}} = P''_{\text{SiCl}_4} + P''_{\text{SiHCl}_3} + P''_{\text{SiH}_2\text{Cl}_2} + P''_{\text{SiH}_3\text{Cl}} \quad (1.1)$$

This method of equalization of sums of the several partial pressures is used to express a common contribution from the several reactions, but such an equilibrium condition is inaccurate, as it allows the appearance of

$$P'_{\text{SiCl}_4} \neq P''_{\text{SiCl}_4}; \quad P'_{\text{SiHCl}_3} \neq P''_{\text{SiHCl}_3}; \quad P'_{\text{SiH}_2\text{Cl}_2} \neq P''_{\text{SiH}_2\text{Cl}_2}; \\ P'_{\text{SiH}_3\text{Cl}} \neq P''_{\text{SiH}_3\text{Cl}} \quad (1.2)$$

Because eq 1.1 requires only that the sums of the partial pressures are equal, not that the partial pressures themselves are equal with a one-to-one correspondence. This results in the appearance of two partial pressures: one is in equilibrium with the reaction tube wall; the other is in equilibrium with the Si activity in the epilayer. In one equilibrium system, there exist two equilibrium partial pressures for one species; this is obviously absurd. An equilibrium system requires that

$$P'_{\text{SiCl}_4} = P''_{\text{SiCl}_4}; \quad P'_{\text{SiHCl}_3} = P''_{\text{SiHCl}_3}; \quad P'_{\text{SiH}_2\text{Cl}_2} = P''_{\text{SiH}_2\text{Cl}_2}; \\ P'_{\text{SiH}_3\text{Cl}} = P''_{\text{SiH}_3\text{Cl}} \quad (1.3)$$

Obviously, by each equation in formula 1.3, we can find one Si activity. However, whether the four Si activities thus obtained are equal or not turns out actually to be whether the equilibria of all reactions in one system can be compatible or not. This is an important omission of universal significance for the complex system. Just because chemical thermodynamics lacks this link, scientists are short of guidelines while tackling the algorithm. Therefore, that inaccuracy is not something any individual scientist should be responsible for. This point can be seen from the fact that the negligence of the algorithm was not discovered for a long period of time; on the contrary, scholars in various countries are always imitating and developing it.⁵⁻⁷ Therefore, what we should do first is to find the missing link and to solidify the equilibrium theory for the complex system.

Compatibility Relationship among the Equilibria of All the Reactions in a Complex System

As stated above, arbitrarily choosing one equation from formula 1.3 and then calculating according to it, we can find Si activity. However, this will result in other silane chlorides' formation reactions and their dissociation reactions becoming nonindependent. Thus, for the general case, a universal problem before us is whether an equilibrium composition found by the independent reaction equations can make the nonindependent reactions therein equilibrating or not. The proof of the compatibility relationship is exactly an answer to the problem (refer to Appendix A). The concept of the compatibility of reaction equilibria can be stated as follows:

In an equilibrium complex system, each species can only contribute one and the same quantity (its equilibrium quantity) to the different equilibria of the various reactions involving it; yet even under this restriction, every equilibrium constant is satisfied, and all the reaction equilibria coexist compatibly in the system.

The compatibility relationship is a representation of the actual case of an equilibrium complex system and is of great significance. Let us imagine a complex system: if an equilibrium composition determined by its independent reactions could not satisfy its nonindependent reactions, such nonindependent reactions then would, through their respective reactions, change that composition, making themselves tend to their respective equilibria; in this way, its independent reactions would lose their original equilibria, and said system could not have a stable

equilibrium state. Therefore, the content of said relationship and the fact that it can be proved by thermodynamics turns out to be a representation of perfection and rigor of thermodynamics. Thermodynamics affirms first that all chemical systems always tend to equilibrium when environmental conditions are fixed; then, said relationship reproduces and proves this point on a level of quantitative calculation of the suitability of the equilibrium composition of a system to its every reaction equilibrium.

Solidifying the Equilibrium Theory for the Complex System

In the past, many people thought that in an equilibrium complex system every reaction therein must surely be in equilibrium. On the basis of this belief, people arbitrarily choose independent reactions to calculate the equilibrium composition. But all this has no theoretic basis because thermodynamics' equilibrium criterion is for a system, not for each reaction in the system. To make chemical thermodynamics more rigorous, previous work has proved that when a system of several independent reactions has reached equilibrium, each independent reaction therein has its relation $\sum \gamma_i \mu_i = 0$.⁸ However, such a proof is incomplete because in the proof the independent reactions are arbitrarily chosen. There naturally arise such problems about the system's equilibrium composition found by the independent reactions thus arbitrarily chosen, i.e., whether it can make all the rest of the reactions equilibrating or not, in other words, whether it is a real equilibrium composition or not, whether thus arbitrarily choosing is permissible or not. The present proof stated in Appendix A gives an answer to the problems. A combination of the two proofs extends the equilibrium criterion to each reaction of a complex system and, thus, constitutes the equilibrium theory for the system.

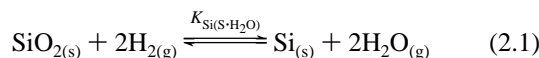
On a practical side, there can hardly be any system of a single chemical process, because a reaction usually has byproducts of many species and because the reactor and the impurities in the raw materials also take part in reaction.

Equivalence Principle of Reaction Approaches

Let us consider the aforestated calculation of Si contamination. Since the actual case of an equilibrium complex system is that all the reactions are, respectively, in equilibrium, we should not employ the algorithm of the sums of the several partial pressures, as expressed in formula 1.1, but should arbitrarily choose one reaction forming Si and then calculate according to the equilibrium conditions. As for other Si-containing species' influence on Si contamination, it can be fully reflected by the quantity of the water formed in the tube wall reactions. Such an algorithm originating from the compatibility concept is of universal significance and can be generalized as an equivalence principle:

In a complex system, a certain species can usually be simultaneously formed by many chemical reactions; when the system has reached equilibrium under fixed environmental conditions, the equilibrium quantity of said species calculated according to each chemical equation of these reactions will be equal and the various reaction approaches will be equivalent, provided that for all the reactants and all the other products of these reactions their equilibrium quantities in the system are respectively taken as corresponding knowns for the calculations.

Now that any one of reactions forming Si can be chosen, naturally, the simplest is to choose the reaction of SiO_2 , because SiO_2 is always a high-purity solid, while the equilibrium quantities of other silicides are variable.



This reaction shows that solid SiO_2 is reduced by hydrogen, forming solid Si. Such Si can by no means drop onto the epilayer while the Si activity α_{Si} calculated according to it is equal to the α_{Si} calculated according to a volatile silicides' reaction; that is, they are equivalent. This reaction formula can be called an equivalent formula. The merit of this formula is that we can be liberated from cumbersome paths of the Si contamination and directly focus on the essence of the problem. Herefrom, we can obtain

$$\alpha_{\text{Si}} = K_{\text{Si(s-H}_2\text{O)}} \frac{P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2} \quad (2.2)$$

Here, we can immediately arrive at three conclusions: (1) at a fixed P_{H_2} , increasing the partial pressure of water will inhibit Si contamination,

$$\alpha_{\text{Si}} \propto \frac{1}{P_{\text{H}_2\text{O}}^2}$$

(2) at a fixed $P_{\text{H}_2\text{O}}$, decreasing the partial pressure of hydrogen will also inhibit Si contamination,

$$\alpha_{\text{Si}} \propto P_{\text{H}_2}^2$$

(3) the equilibrium partial pressure of HCl has no direct influence on the Si contamination from the tube wall.

The Si contamination model was proposed as early as 1971,² but as the algorithm previously used is imperfect, conclusion 2 was reached as late as 7 years after.⁶ Moreover, up to now, there are still international views completely opposite conclusion 3. However, these are instantaneously clear when viewed from the equivalent formula, which tells the very wonder of it. At $P_{\text{H}_2} = 1$ (usually the partial pressures of other species are very small), formula 2.2 can be reduced to

$$\alpha_{\text{Si}} = K_{\text{Si(s-H}_2\text{O)}} \frac{1}{P_{\text{H}_2\text{O}}^2} \quad (2.3)$$

Now we refer to the algorithm of the pioneers:^{2,4}

$$\alpha_{\text{Si}} = \frac{K_{25}P_{\text{HCl}}^4 + K_{26}P_{\text{HCl}}^3 + K_{27}P_{\text{HCl}}^2 + K_{28}P_{\text{HCl}}}{(K_{33}P_{\text{HCl}}^4 + K_{34}P_{\text{HCl}}^3 + K_{35}P_{\text{HCl}}^2 + K_{36}P_{\text{HCl}})P_{\text{H}_2\text{O}}^2} \quad (\text{B.1})$$

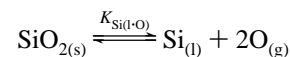
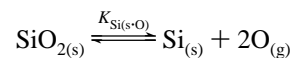
In comparison, what a simple formula it is!

In the recent 20–30 years, notable scholars of various countries considered different reactions introducing Si contamination in the processes of preparation and purification of various materials and established corresponding calculation formulas of different forms. Now that the calculations are all based on the assumption of local equilibrium or of thermodynamic equilibrium and the contamination sources are all SiO_2 , all the calculations can be done by following an identical reaction path and can be made uniform in the light of said principle. In Appendix B, we will prove that all the solid-state Si contamination (such as Si contamination in GaAs) activity $\alpha_{\text{Si(s)}}$ and all the liquid-state Si contamination (such as Si contamination in liquid Ga) activity $\alpha_{\text{Si(l)}}$ can be respectively standardized into

$$\alpha_{\text{Si(s)}} = K_{\text{Si(s-O)}} \frac{1}{P_{\text{O}}^2} \quad (2.4)$$

$$\alpha_{\text{Si(l)}} = K_{\text{Si(l-O)}} \frac{1}{P_{\text{O}}^2} \quad (2.5)$$

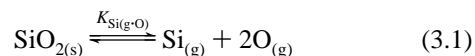
wherein P_{O} is the partial pressure of oxygen atoms in the reactor and $K_{\text{Si(s-O)}}$ and $K_{\text{Si(l-O)}}$ are respectively the equilibrium constants of the following two reactions:



This also proved that only the oxygen can inhibit Si contamination. HCl inhibition of Si contamination results from oxygen. With the increase of P_{HCl} , the oxygen also increases owing to tube wall reactions. This clarification of inhibition mechanism is of importance, because in all the cases that we use the quartz reactor, at high temperature, to prepare high-purity materials, the decrease of Si contamination is always desired.^{9,10}

Mutual Inhibition Relation between Silicon and Oxygen Impurities

In the GaAs VPE process, there exists dissociation of SiO_2 (the quartz reaction tube) at high temperature:



In this reaction, the quantities of $\text{Si}_{(g)}$ and $\text{O}_{(g)}$ formed are very small. Few Si contaminations or few O contaminations result from this reaction. However, on the basis of said principle, it is absolutely equivalent to other reaction approaches. The dissociation equilibrium is

$$P_{\text{Si(g)}}P_{\text{O(g)}}^2 = K_{\text{Si(g-O)}} \quad (3.2)$$

In a certain range of $P_{\text{Si(g)}}$ or of $P_{\text{O(g)}}$, the silicon incorporation and oxygen incorporation are proportional to $P_{\text{Si(g)}}$ and $P_{\text{O(g)}}$, respectively:

$$\alpha_{\text{Si}} = K_{\text{Si(g-s)}}P_{\text{Si(g)}}, \quad \alpha_{\text{O}} = K_{\text{O(g-s)}}P_{\text{O(g)}} \quad (3.3)$$

Then we have

$$\alpha_{\text{Si}}\alpha_{\text{O}}^2 = K_{\text{Si(g-s)}}K_{\text{O(g-s)}}^2K_{\text{Si(g-O)}} = K_{\text{Si-O(s)}} \quad (3.4)$$

This result is of universal significance; the importance of it lies in the fact that it connects together the contamination quantities of two extremely important impurities. For convenience sake, it is designated as the silicon–oxygen mutual inhibition formula. Without said principle, there was not a way to solve this kind of problem, because multiple species containing Si (such as SiO , SiH_4 , SiH_3Cl , SiH_2Cl_2 , SiHCl_3 , SiCl_4 , SiCl_2) and multiple species containing O (such as H_2O , O_2 , As_2O_5 , As_2O_3 , Ga_2O , GaO , SiO) simultaneously make contributions to Si and O contaminations, respectively. These contributors react with each other, thus tying in so many reactions to a dazzling extent. Said principle, at our wits' end, lends us a clue to the exact solution of the problem, a problem of the functional relation among species' equilibrium quantities. To show formula 3.4 by illustration, we take the oxygen atom partial

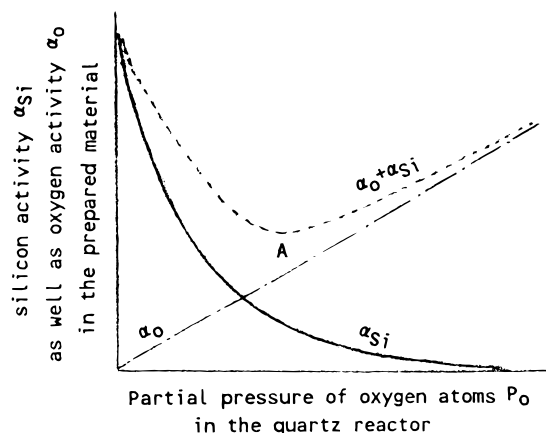


Figure 2. Schematic diagram of formula 3.4.

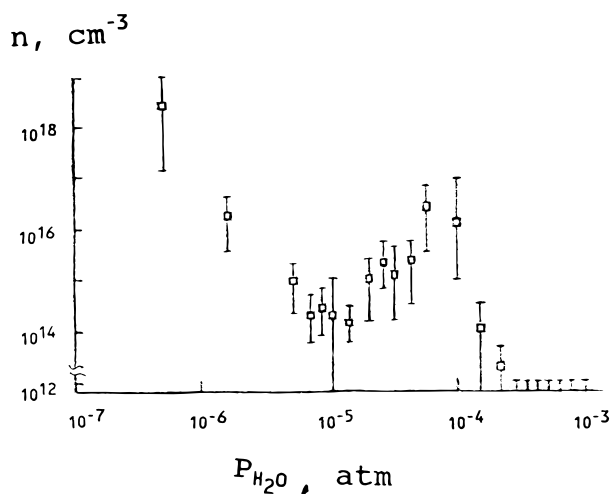


Figure 3. Maksimov's et al. water addition experiment: electron concentration in the GaAs layer vs water vapor content in the gas phase.

pressure P_O as the abscissa and the activity of the impurity in the epilayer as the ordinate. Then, in the case of not too large a P_O , we obtain one straight line of oxygen contamination α_O increasing along with P_O and another curve of silicon contamination α_{Si} abruptly decreasing with the increase of P_O , while the curve of $\alpha_O + \alpha_{Si}$ represents the sum of the contamination quantities of the two:

$$\alpha_O + \alpha_{Si} = K_{O(g-s)} P_{O(g)} + K_{Si(g-s)} \frac{K_{Si-O(s)}}{P_{O(g)}^2} \quad (3.5)$$

or

$$\alpha_O + \alpha_{Si} = \frac{K_{Si-O(s)}}{P_{O(g)}^2} + \alpha_O \quad (3.6)$$

or

$$\alpha_O + \alpha_{Si} = \alpha_{Si} + \left(\frac{K_{Si-O(s)}}{\alpha_{Si}} \right)^{1/2} \quad (3.7)$$

As the exact values of $K_{Si(g-s)}$ and $K_{O(g-s)}$ are unknown, so there is no scale on the coordinate of Figure 2. As the silicon and oxygen are considered to be donors, the curve $\alpha_O + \alpha_{Si}$ has the same trend as the result of the water addition experiment by Maksimov et al.¹¹ (as shown in Figure 3).

There is a lowest point A in curve $\alpha_O + \alpha_{Si}$; calculation shows that at this point the contamination quantity of silicon is

not equal to that of oxygen, $\alpha_O = (2K_{Si-O(s)})^{1/3}$, $\alpha_{Si} = (K_{Si-O(s)}/4)^{1/3}$. It is unknown whether the contamination quantity of silicon and that of oxygen both within a material having the highest mobility and prepared with the quartz reactor should be at point A or not, and it is unknown whether today's practice has reached point A or not.

For other reactor, crucible, encapsulating, or isolating materials (such as BN, alumina¹²), the corresponding atom contaminations from such a contacted compound can be discussed in the same way as above.

Concluding Remarks

Because in an equilibrium complex system all the reaction equilibria are compatible, we can arbitrarily choose the independent reactions to calculate the equilibrium composition. On the same grounds, there exists the equivalence principle. The compatibility relationship turns out to be the basis of various algorithms for the complex system and is a key to our comprehending and analyzing the system.

The rationale of the arbitrary choice and the rationale of said principle are of an identical origin: said relationship. However in the past, people only knew the former, but did not know the latter, said principle. It is because at that time the compatibility concept did not exist. So, arbitrarily choosing the independent reactions is but a customary practice without a logic basis. This shows the importance of the conception of said relationship.

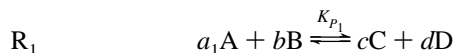
The compatibility concept is an indispensable link in the logic chain of chemical thermodynamics. It will make the existing chemical thermodynamics more harmonic, more rigorous, and more perfect.

Appendix A: Proof of the Compatibility Relationship

As the equilibrium composition of a complex system is determined by the independent reactions, naturally, it satisfies their equilibrium constants. The rest we need to prove is that it can make the nonindependent reactions therein equilibrious.

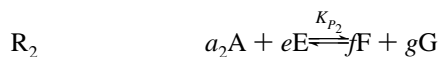
Proof Method 1. A nonindependent reaction R_3 can be expressed by linearly combining two independent reactions R_1 and R_2 as follows: $R_3 = R_1 + K_{(A1.1)} R_2$, where $K_{(A1.1)}$ is a coefficient; then $\Delta G_{TR3} = \Delta G_{TR1} + K_{(A1.1)} \Delta G_{TR2}$, where ΔG_T is the free energy change in reaction at temperature T . For R_1 and R_2 , the equilibrium composition determined by themselves naturally results in $\Delta G_{TR1} = 0$, and in $\Delta G_{TR2} = 0$; so $\Delta G_{TR3} = 0$, i.e., for R_3 , its equilibrium relationship is also satisfied.

Proof Method 2. Consider an ideal gas system. The two given independent reactions are as follows:



which is already in equilibrium, having

$$\frac{P_C^c P_D^d}{P_A^{a_1} P_B^b} = K_{P1} \quad (A1.1)$$



which is also already in equilibrium, having

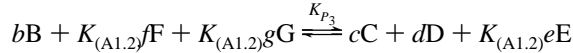
$$\frac{P_F^f P_G^g}{P_A^{a_2} P_E^e} = K_{P2} \quad (A1.2)$$

Provided that $a_1/a_2 = K_{(A1.2)}$, the nonindependent reaction R_3

constituted by the two is equal to

$$R_3 = R_1 - K_{(A1.2)}R_2 \quad (A1.3)$$

Its specific reaction formula is



What is to be proved is the following: the equilibrium composition satisfying the equilibrium constants of the two also satisfies that of R_3 ,

$$\frac{P_C^c P_D^d P_E^{ek(A1.2)}}{P_B^b P_F^{K(A1.2)} P_G^{gK(A1.2)}} = K_{P_3}$$

Firstly, we calculate $(A1.1)/(A1.2)^{K_{(A1.2)}}$ in order that the equilibrium composition is “implanted” into the first member of the equilibrium expression of R_3 , obtaining

$$\frac{P_C^c P_D^d P_E^{ek(A1.2)}}{P_B^b P_F^{K(A1.2)} P_G^{gK(A1.2)}} = \frac{K_{P_1}}{(K_{P_2})^{K_{(A1.2)}}} \quad (A1.4)$$

Then it is to be proved that $K_{P_1}/(K_{P_2})^{K_{(A1.2)}}$ is equal to the equilibrium constant K_{P_3} of the reaction R_3 . Because

$$-RT \ln K_{P_1} = \Delta G_{TR_1}^\circ \quad \text{and} \quad -RT \ln K_{P_2} = \Delta G_{TR_2}^\circ$$

where ΔG° is the standard free energy change in reaction at temperature T , therefore, from eq A1.3, we have

$$\Delta G_{TR_3}^\circ = \Delta G_{TR_1}^\circ - K_{(A1.2)} \Delta G_{TR_2}^\circ = -RT \ln \frac{K_{P_1}}{(K_{P_2})^{K_{(A1.2)}}} = -RT \ln K_{P_3}$$

That is actually $K_{P_1}/(K_{P_2})^{K_{(A1.2)}} = K_{P_3}$, and the proof comes to an end.

This proof stated above can be generalized to the case that a nonindependent reaction can be expressed by linearly combining more than two independent reactions and be generalized to other equilibrium constant expressions K_c and K_x , to an ideal solution, to a nonideal system, and to the case where a condensed substance takes part in the reaction.

Appendix B: Uniformity of Various Schools' Algorithms for the Equilibrium Quantity of Si Contamination

In the following, several representative algorithms are taken as examples.

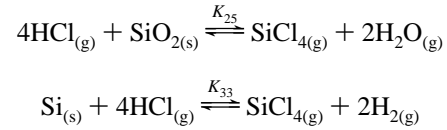
For VPE GaAs, DiLorenzo et al.² and Rai-Choudhury⁴ each obtained a result of the same form simultaneously:

$$\alpha_{Si} = \frac{K_{25}P_{HCl}^4 + K_{26}P_{HCl}^3 + K_{27}P_{HCl}^2 + K_{28}P_{HCl}}{(K_{33}P_{HCl}^4 + K_{34}P_{HCl}^3 + K_{35}P_{HCl}^2 + K_{36}P_{HCl})P_{H_2O}^2} \quad (B.1)$$

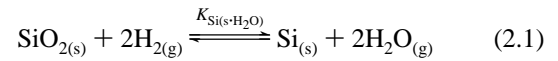
The difference between the two is that DiLorenzo et al. took the source and substrate temperatures as the temperatures of the reactions generating various silane chlorides and of the reactions dissociating them respectively, while Rai-Choudhury used only substrate temperature as the temperature of these two kinds of reactions. The former actually used a model of local noncomplete equilibrium. The reason for it is obvious: in the source region, more silane chlorides are generated at a higher

temperature, but in the course of their moving to the substrate region the nonequilibria between them and the quartz tube wall will take place as the temperature is falling. That case can hardly exist in reality since hydrolysis rates of silane chlorides are very fast. Weiner¹³ ever predicted that along with the drop in temperature of the gas flow in the reaction tube there would be deposited fine grains of SiO_2 . Therefore, the algorithm of only the substrate temperature is more reasonable.

In ref 4, K_{25} and K_{33} are the equilibrium constants of the following two reactions, respectively:



Obviously, K_{25}/K_{33} is the equilibrium constant $K_{Si(s) \cdot H_2O}$ of the reaction obtained by subtraction of the latter from the former:



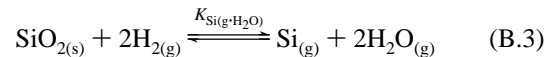
That is, $K_{25}/K_{33} = K_{Si(s) \cdot H_2O}$. So, $K_{25} = K_{33}K_{Si(s) \cdot H_2O}$. The same method can be used to prove $K_{26} = K_{34}K_{Si(s) \cdot H_2O}$; $K_{27} = K_{35}K_{Si(s) \cdot H_2O}$; $K_{28} = K_{36}K_{Si(s) \cdot H_2O}$. Substituting the above four equations into formula B.1 and then reducing the result, we will have

$$\alpha_{Si} = K_{Si(s) \cdot H_2O} \frac{1}{P_{H_2O}^2} \quad (2.3)$$

For undoped and Si-doped VPE GaAs, P. Küpper et al.⁵ obtained the result

$$P_{Si} = \frac{\sum K_{ln} K_{4n}}{4P_{H_2O}^2} \quad (B.2)$$

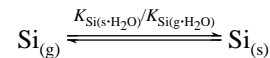
Using the same method, we can prove that each term in the sum $\sum K_{ln} K_{4n}$ is equal to the equilibrium constant $K_{Si(g) \cdot H_2O}$ of the overall reaction



Thus, $\sum K_{ln} K_{4n}$, the sum of four terms, equaling $4K_{Si(g) \cdot H_2O}$, clearly shows that the algorithm of adding up the results of four contamination approaches gives exactly four times the result of one approach; therefore $\sum K_{ln} K_{4n}$ should be divided by 4. This shows the accuracy of said equivalence principle. Substituting our results into eq B.2, we obtain

$$P_{Si} = \frac{K_{Si(g) \cdot H_2O}}{P_{H_2O}^2} \quad (B.4)$$

Subtracting reaction formula B.3 from formula 2.1, we obtain



That is

$$\frac{\alpha_{Si}}{P_{Si}} = \frac{K_{Si(s) \cdot H_2O}}{K_{Si(g) \cdot H_2O}}$$

Multiplying this equation by formula B.4 and then reducing the

result, we have

$$\alpha_{\text{Si}} = \frac{K_{\text{Si(s}\cdot\text{H}_2\text{O)}}}{P_{\text{H}_2\text{O}}^2}$$

which is the same as formula 2.3.

The above formulas of DiLorenzo et al., Rai-Choudhury, and P. Küpper et al. all relate to the open flow quartz system with $P_{\text{H}_2} \approx 1$; therefore P_{H_2} is negligible; if not, for the general case, formula 2.3 will turn into the form of formula 2.2:

$$\alpha_{\text{Si}} = K_{\text{Si(s}\cdot\text{H}_2\text{O)}} \frac{P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2} \quad (2.2)$$

Hisashi Seki et al. studied a GaAs VPE system where the mixture of inert gas and hydrogen is used as the carrier gas and derived a final result wherein only SiCl_4 is considered:⁶

$$\alpha_{\text{Si}} = \frac{K_4 K_8 F^2}{(P_{\text{H}_2\text{O}}^0 + 2P_{\text{SiCl}_4})^2} \quad (\text{B.5})$$

As explained above, the algorithm of two temperatures, i.e., the source and substrate temperatures, is not accurate. Provided that the temperatures of all the reactions are considered to be the substrate temperature, the same method can be used to prove $K_4 K_8 = K_{\text{Si(s}\cdot\text{H}_2\text{O)}}$. Besides, $P_{\text{H}_2\text{O}}^0 + 2P_{\text{SiCl}_4} = P_{\text{H}_2\text{O}}$. As for F , it means in their paper⁶ the molar fraction of hydrogen in the carrier gas and is introduced on the basis of the consideration that it approximates the equilibrium partial pressure of hydrogen, P_{H_2} , i.e., $F \approx P_{\text{H}_2}$, thus eq B.5 turns into

$$\alpha_{\text{Si}} = K_{\text{Si(s}\cdot\text{H}_2\text{O)}} \frac{P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2}$$

For the InP hydride VPE system, Jones⁷ gave the result

$$\alpha_{\text{Si}} = \frac{P_{\text{H}_2\text{O}}}{2 \left(\frac{P_{\text{HCl}}^2 P_{\text{H}_2}^{-1}}{K'_{\text{SiCl}_2}} + \sum \frac{P_{\text{HCl}}^n P_{\text{H}_2}^{2-n}}{K'_{\text{SiCl}_n\text{H}_{4-n}}} \right)} \quad (\text{B.6})$$

The formulas 22 and 26 in his paper⁷ are substituted into eq B.6 to obtain

$$\begin{aligned} \alpha_{\text{Si}} &= \frac{K_{\text{SiCl}_2} P_{\text{HCl}}^2 P_{\text{H}_2} + \sum K_{\text{SiCl}_n\text{H}_{4-n}} P_{\text{HCl}}^n P_{\text{H}_2}^{4-n}}{P_{\text{H}_2\text{O}}^2 \left(\frac{P_{\text{HCl}}^2 P_{\text{H}_2}^{-1}}{K'_{\text{SiCl}_2}} + \sum \frac{P_{\text{HCl}}^n P_{\text{H}_2}^{2-n}}{K'_{\text{SiCl}_n\text{H}_{4-n}}} \right)} \\ &= \frac{P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2} \left(\frac{K_{\text{SiCl}_2} P_{\text{HCl}}^2 P_{\text{H}_2} + \sum K_{\text{SiCl}_n\text{H}_{4-n}} P_{\text{HCl}}^n P_{\text{H}_2}^{4-n}}{K'_{\text{SiCl}_2}^{-1} P_{\text{HCl}}^2 P_{\text{H}_2} + \sum K'_{\text{SiCl}_n\text{H}_{4-n}}^{-1} P_{\text{HCl}}^n P_{\text{H}_2}^{4-n}} \right) \end{aligned}$$

The same method can be used to prove that

$$K_{\text{SiCl}_2} K'_{\text{SiCl}_2} = K_{\text{Si(s}\cdot\text{H}_2\text{O)}}, \quad \text{i.e.,} \quad K_{\text{SiCl}_2} = K_{\text{Si(s}\cdot\text{H}_2\text{O)}} K'_{\text{SiCl}_2}^{-1}$$

There exist similar relationships for SiH_3Cl , SiH_2Cl_2 , SiHCl_3 , and SiCl_4 . Substituting them into the above formula and then reducing the result, we have

$$\alpha_{\text{Si}} = K_{\text{Si(s}\cdot\text{H}_2\text{O)}} \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}^2}$$

In 1972, Weiner made a detailed calculation¹³ on Si contamination of liquid gallium in an open flow quartz system. The uniformity we are making relates only to the algorithms for the equilibrium quantity of Si contamination, not to those for the Si contamination rates he studied. Weiner's model involves tube wall reactions only taking place upstream from the Ga boat, while at the boat, there is only the consumption of the silicides formed in those tube wall reactions, without the supplementation of them. Thus, the silicides will not remain, at the boat, in equilibria with the quartz tube wall. Therefore, this is but a local noncomplete equilibrium model. So, the formulas of case A and case C-1¹³ do not belong to formula 2.2. As for case B and case C-2, because he has taken into consideration the equilibrium of the reaction at the boat, $4\text{Ga}_{(\text{l})} + \text{SiO}_{2(\text{s})} = 2\text{Ga}_2\text{O}_{(\text{g})} + \text{Si}_{(\text{l})}$, the calculation of the steady-state values was inadvertently based on the local complete equilibrium model, so these two formulas can be uniformized.

For case B

$$\frac{dx_i}{dt} = \frac{F}{2RTN_{\text{Ga}}} \left[\frac{K_3 K_4^{1/2} + K_3 K_2 K_4^{1/2}}{K_2 x_{\text{Si}}^{1/2}} - K_4^{1/2} x_{\text{Si}}^{1/2} - P_{\text{H}_2\text{O}}^0 \right]$$

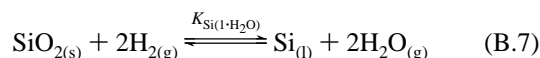
When Si in gallium reaches equilibrium, $dx_{\text{Si}}/dt = 0$,

$$\begin{aligned} \frac{K_3 K_4^{1/2} + K_3 K_2 K_4^{1/2}}{K_2 x_{\text{Si}}^{1/2}} - K_4^{1/2} x_{\text{Si}}^{1/2} - P_{\text{H}_2\text{O}}^0 &= 0 \\ \frac{K_3 K_4^{1/2}}{K_2 x_{\text{Si}}^{1/2}} &= K_4^{1/2} x_{\text{Si}}^{1/2} + P_{\text{H}_2\text{O}}^0 - \frac{K_3 K_4^{1/2}}{x_{\text{Si}}^{1/2}} \end{aligned}$$

In accordance with the original calculation,¹³

$$\frac{K_3 K_4^{1/2}}{K_2} = K_{\text{Si(1}\cdot\text{H}_2\text{O)}}^{1/2}$$

$K_{\text{Si(1}\cdot\text{H}_2\text{O)}}$ is the equilibrium constant of the reaction



and

$$K_4^{1/2} x_{\text{Si}}^{1/2} = P_{\text{SiO}}, \quad \frac{K_3 K_4^{1/2}}{x_{\text{Si}}^{1/2}} = P_{\text{Ga}_2\text{O}}$$

The above equation turns into

$$\frac{K_{\text{Si(1}\cdot\text{H}_2\text{O)}}^{1/2}}{x_{\text{Si}}^{1/2}} = P_{\text{SiO}} + P_{\text{H}_2\text{O}}^0 - P_{\text{Ga}_2\text{O}} = P_{\text{H}_2\text{O}}$$

$$x_{\text{Si}}^{1/2} = \frac{K_{\text{Si(1}\cdot\text{H}_2\text{O)}}^{1/2}}{P_{\text{H}_2\text{O}}}$$

Because $P_{\text{H}_2} \approx 1$, P_{H_2} has been neglected; if P_{H_2} is taken into consideration, the formula will turn into

$$x_{\text{Si}}^{1/2} = K_{\text{Si}(1\cdot\text{H}_2\text{O})}^{1/2} \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

Provided that $\alpha_{\text{Si}(l)}$ is used to represent x_{Si} and then squaring the above equation, we obtain

$$\alpha_{\text{Si}(l)} = K_{\text{Si}(1\cdot\text{H}_2\text{O})} \frac{P_{\text{H}_2}^2}{P_{\text{H}_2\text{O}}^2} \quad (\text{B.8})$$

For case C-2, the result derived by Weiner¹³ reads as

$$\frac{dx_{\text{Si}}}{dt} = \frac{F}{2RTN_{\text{Ga}}} \left[\frac{K_3 K_4^{1/2} \left(1 + \frac{1}{K_2}\right)}{x_{\text{Si}}^{1/2}} - K_4^{1/2} x_{\text{Si}}^{1/2} - P_{\text{H}_2\text{O}}^0 - 2x_{\text{Si}} \left(\frac{P_{\text{GaCl eq}}}{K_9} + \frac{P_{\text{GaCl eq}}^2}{K_{10}} + \frac{P_{\text{GaCl eq}}^3}{K_{11}} + \frac{P_{\text{GaCl eq}}^4}{K_{12}} \right) \right]$$

When $dx_{\text{Si}}/dt = 0$, we have

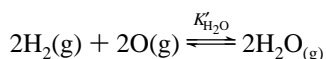
$$\frac{K_3 K_4^{1/2}}{K_2 x_{\text{Si}}^{1/2}} = K_4^{1/2} x_{\text{Si}}^{1/2} + P_{\text{H}_2\text{O}}^0 - \frac{K_3 K_4^{1/2}}{x_{\text{Si}}^{1/2}} + 2x_{\text{Si}} \left(\frac{P_{\text{GaCl eq}}}{K_9} + \frac{P_{\text{GaCl eq}}^2}{K_{10}} + \frac{P_{\text{GaCl eq}}^3}{K_{11}} + \frac{P_{\text{GaCl eq}}^4}{K_{12}} \right)$$

Following the example of case B, we have

$$\begin{aligned} \frac{K_{\text{Si}(1\cdot\text{H}_2\text{O})}^{1/2}}{x_{\text{Si}}^{1/2}} &= P_{\text{SiO}} + P_{\text{H}_2\text{O}}^0 - P_{\text{Ga}_2\text{O}} + 2(P_{\text{SiH}_3\text{Cl}} + P_{\text{SiH}_2\text{Cl}_2} + P_{\text{SiHCl}_3} + P_{\text{SiCl}_4}) \\ &= P_{\text{H}_2\text{O}} \end{aligned}$$

Taking similar steps as above, we can reduce it into the same form as eq B.8.

Formula 2.2 and formula B.8 both contain the factor $P_{\text{H}_2}^2/P_{\text{H}_2\text{O}}^2$, while $P_{\text{H}_2}^2/P_{\text{H}_2\text{O}}^2 = 1/K'_{\text{H}_2\text{O}} P_{\text{O}}^2$; this can be seen from the reaction

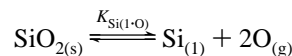
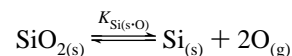


(here, we write O for O₂ in order to express the influence of P_{O} on α_{Si}). Substituting the above relationship into formulas 2.2 and B.8 and assigning a subscript (s) to the α_{Si} in formula 2.2 so as to show that it is solid-state Si contamination, the two formulas will respectively turn into

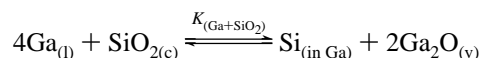
$$\alpha_{\text{Si}(s)} = \frac{K_{\text{Si}(s\cdot\text{H}_2\text{O})}}{K'_{\text{H}_2\text{O}}} \frac{1}{P_{\text{O}}^2} = K_{\text{Si}(s\cdot\text{O})} \frac{1}{P_{\text{O}}^2} \quad (2.4)$$

$$\alpha_{\text{Si}(l)} = \frac{K_{\text{Si}(1\cdot\text{H}_2\text{O})}}{K'_{\text{H}_2\text{O}}} \frac{1}{P_{\text{O}}^2} = K_{\text{Si}(1\cdot\text{O})} \frac{1}{P_{\text{O}}^2} \quad (2.5)$$

$K_{\text{Si}(s\cdot\text{H}_2\text{O})}/K'_{\text{H}_2\text{O}}$ and $K_{\text{Si}(1\cdot\text{H}_2\text{O})}/K'_{\text{H}_2\text{O}}$ are the equilibrium constants of the following two overall reactions, respectively:



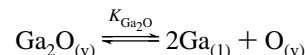
Cochran et al.¹⁴ studied the Si contamination in the process of HB GaAs. For the Si contamination of liquid Ga during the processing, their calculation starts from the reaction



Herefrom they obtain

$$\alpha_{\text{Si}(l)} = \frac{K_{(\text{Ga}+\text{SiO}_2)}}{P_{\text{Ga}_2\text{O}}^2}$$

Because there exists the dissociation of Ga₂O,



$P_{\text{Ga}_2\text{O}}$ can be expressed by P_{O} ; hence,

$$\alpha_{\text{Si}(l)} = K_{(\text{Ga}+\text{SiO}_2)} K_{\text{Ga}_2\text{O}}^2 \frac{1}{P_{\text{O}}^2} = K_{\text{Si}(1\cdot\text{O})} \frac{1}{P_{\text{O}}^2}$$

As for the Si contamination in GaAs, the similar treatment can be made herewith and the result is the same as formula 2.4.

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