Application of the Compatibility Relationship[1] in Seeking a Functional Relationship among Species' Equilibrium Quantities in Complex Systems

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A new algorithm, representing an important advance in determination of the functional relationship, is first reported here. The algorithm is very useful and convenient for analyzing the incorporation of impurities. To show how the algorithm works, two early and well-known vapor phase epitaxy (VPE) experiments—Ashen's (Ashen, D. J.; Dean, P. J.; Hurle, D. T. J.; Mullin, J. B.; Royle, A.; White, A. M. Gallium Arsenide and Related Compounds, Institute of Physics Conference Series 24, 1974; Institute of Physics: London, 1975; p 229.), involving the doping of silicon and DiLorenzo's (DiLorenzo, J. V. *J. Cryst. Growth* **1972**, *17*, 189.), involving the mole fraction effect—are calculated to find the functional relationship between the Si contamination and the partial pressure of HCl. The calculated curves agree with the experimental results. A conclusion that the calculated values are greater than the true values has been drawn.

Studying a complex system, we are concerned with the species of interest, especially its quantity that is formed in the reaction system, and try to tell which species in the system has direct influence upon said quantity and which species have indirect influences. The formulation of these influences are of importance both in theory and practice, because the formula will show us conditions under which the optimum of said quantity can be achieved. But, without the compatibility relationship, there would be no correct algorithm for solving this kind of problem, a problem of functional relationship among species' equilibrium quantities. The following two examples will make this clear.

Example 1. Ashen et al.'s Experiment of Doping Silicon.[2] The conventional AsCl₃−Ga−H₂ VPE system is familiar to us (see Figure 1). But, out of the ordinary is that Ashen's experiment lined the quartz reaction tube internally with BN to eliminate the unintentional doping of silicon from the quartz tube. Then, they put silicon into the gallium source (we use $K^\#$ to denote the atom number ratio of the Si to the Ga) to study the influence of HCl on the intentional doping of silicon. The behavior coincident between the intentional and unintentional dopings is evidence to prove that Si is a residual impurity in VPE GaAs.

At the source temperature, AsCl₃ is completely decomposed by H₂, forming HCl, As₄ and As₂. The Si and Ga in the source, in accordance with the ratio $K^\#$, react with HCl, forming SiCl₄, SiHCl₃, SiH₂Cl₂, SiH₃Cl, SiCl₂, GaCl, etc., and entering the vapor phase. The total pressure of these silicides is expressed as $\sum P_{Si(v)}$. Because the formed species contain only one Si or one Ga atom in each molecule, we have $\sum P_{Si(v)} = K^\# P_{GaCl}$. As mentioned above, $\sum P_{Si(v)}$ represents the total volatile silicon. According to DiLorenzo's work (see Ga/As ratio in ref 4), the HCl does not completely react with gallium (about two-thirds reacts with gallium to form GaCl and the rest is free). Hence, we have

$$\sum P_{Si(v)} = K^\# P_{GaCl} = 2\,K^\# P_{HCl} \qquad (1.1)$$

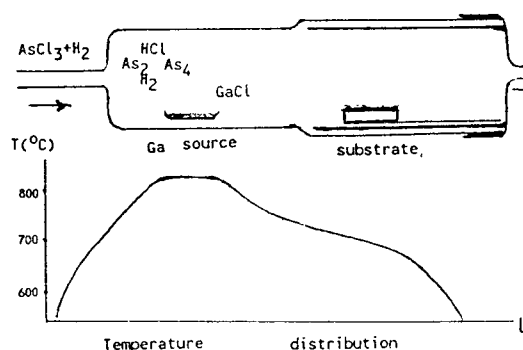and $P_{HCl} \approx P_{AsCl_3}$ where P_{AsCl_3} is the partial pressure of AsCl₃

Figure 1. A conventional AsCl₃-Ga−H₂ VPE system.

in the input hydrogen. In the course of the gas flow moving toward the substrate region, Si does not deposit on the BN tube wall. When the flow moves to the surface of the substrate, only the Si deposition accompanying GaAs deposition on the substrate takes place: we have clearly seen, when using the quartz reaction tube, that there is no GaAs deposition on the tube wall around the substrate. The foregoing statements are the background of the problem we shall deal with below.

At present, the dominant-species algorithm is practically the only way to determine the functional relationship among species' equilibrium quantities. In this algorithm, the species of which the amount is largest is chosen as the dominant, and, for a VPE system, SiCl₄ is often chosen. The process of Si incorporation can be described as
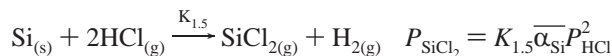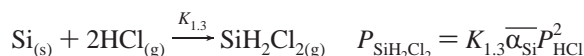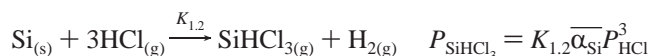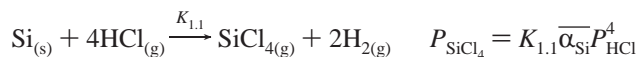
$$SiCl_{4(g)} + 2H_{2(g)} \xrightarrow{K} Si_{(s)} + 4HCl_{(g)}$$
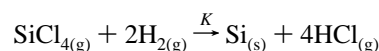
The amount of SiCl₄ is considered to be the total volatile silicon, $\sum P_{Si(v)}$. Then, the activity of Si atoms in the epilayer, α_{Si}, can be found:

$$\alpha_{Si} = K\frac{P_{SiCl_4}P_{H_2}^2}{P_{HCl}^4} = K\frac{\sum P_{Si(v)}}{P_{HCl}^4} = \frac{2KK^\#}{P_{HCl}^3}$$

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where $P_{H_2} \approx 1$, hence P_{H_2} is insignificant. That is an example of a dominant-species algorithm. The above analysis, though simple, shows us that the Si contamination can be inhibited by HCl. This is important for quality control. Seeking function among species' equilibrium quantities is useful. But α_{Si} is not inversely proportional to P_{HCl}^3. The dominant-species algorithm is problematic, especially in those cases in which the dominant species changes; the replacement of one dominant species by another usually leads to a large error. The SiO_2–H_2–HCl system is just such case (see Figure 2).

Figure 2, obtained by calculations, shows the two typical cases in the P_{HCl} range of interest (10^{-3}–10^{-2} atm). With regard to the thermodynamic data used for the calculations in this paper, all are from ref 5 except the standard free energy of $SiH_3Cl_{(g)}$, which is taken from ref 6. The changes in quantities of the silicides with P_{HCl} in this problem is similar to Figure 2. The problem with the algorithm is that it only allows calculation of one species' contribution and that the amount of the species is considered to be the total volatile silicon. It deviates from the fact that multiple species make contributions (e.g., $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, $SiCl_2$, etc., make contributions to α_{Si}). Without the compatibility relationship, there is no way to improve the calculation because no theory can correlate those species with α_{Si}. Now, the compatibility relationship has proven that in an equilibrium complex system, every reaction therein is in equilibrium.[1] The reaction equilibria are compatible. That is to say, those silicides are, respectively, in equilibrium with the silicon atoms in the epilayer. In this way, we can calculate a common contribution made by all of them, because these equilibria reflect their contributions to α_{Si}. The new algorithm just starts from here. Now that they are in equilibrium with the silicon atoms, their quantities can be expressed in α_{Si}.

$$Si_{(s)} + 4HCl_{(g)} \xrightarrow{K_{1.1}} SiCl_{4(g)} + 2H_{2(g)} \qquad P_{SiCl_4} = K_{1.1}\overline{\alpha_{Si}}P_{HCl}^4$$

$$Si_{(s)} + 3HCl_{(g)} \xrightarrow{K_{1.2}} SiHCl_{3(g)} + H_{2(g)} \qquad P_{SiHCl_3} = K_{1.2}\overline{\alpha_{Si}}P_{HCl}^3$$

$$Si_{(s)} + 2HCl_{(g)} \xrightarrow{K_{1.3}} SiH_2Cl_{2(g)} \qquad P_{SiH_2Cl_2} = K_{1.3}\overline{\alpha_{Si}}P_{HCl}^2$$

$$Si_{(s)} + HCl_{(g)} + H_{2(g)} \xrightarrow{K_{1.4}} SiH_3Cl_{(g)} \qquad P_{SiH_3Cl} = K_{1.4}\overline{\alpha_{Si}}P_{HCl}$$

$$Si_{(s)} + 2HCl_{(g)} \xrightarrow{K_{1.5}} SiCl_{2(g)} + H_{2(g)} \qquad P_{SiCl_2} = K_{1.5}\overline{\alpha_{Si}}P_{HCl}^2$$

The HCl consumption in forming the silicides as well as HCl supplementation in dissociating them need not be considered, because in a VPE system, the amounts are too small to vary P_{HCl}. In a deposition, P_{HCl} is fixed. We note here that α_{Si} is not uniform in the epilayer because the amount of deposited Si increases with the move of the gas flow over the horizontal substrate, which results in the total volatile silicon in the vapor phase decreasing and α_{Si} decreasing. For convenience, we take the α_{Si} in the epilayer of the part that lies just on the "halfway line" of the substrate as average, $\overline{\alpha_{Si}}$, where the "halfway line" is a line to which when the gas flow moves, and it just passes half of the surface of the substrate.

The other species, $SiCl_{(g)}$, $SiO_{(g)}$, $SiH_{4(g)}$, and $Si_{(g)}$, are negligible, but the quantity of Si atoms incorporated into the epilayer should be taken into consideration. Let S represent the growth area of the substrate, $\mu_{(HCl)}$ the growth rate per unit time, ρ the atomic density of GaAs; as for the activity coefficient of the Si atoms, we consider it to be 1 as other authors have done;
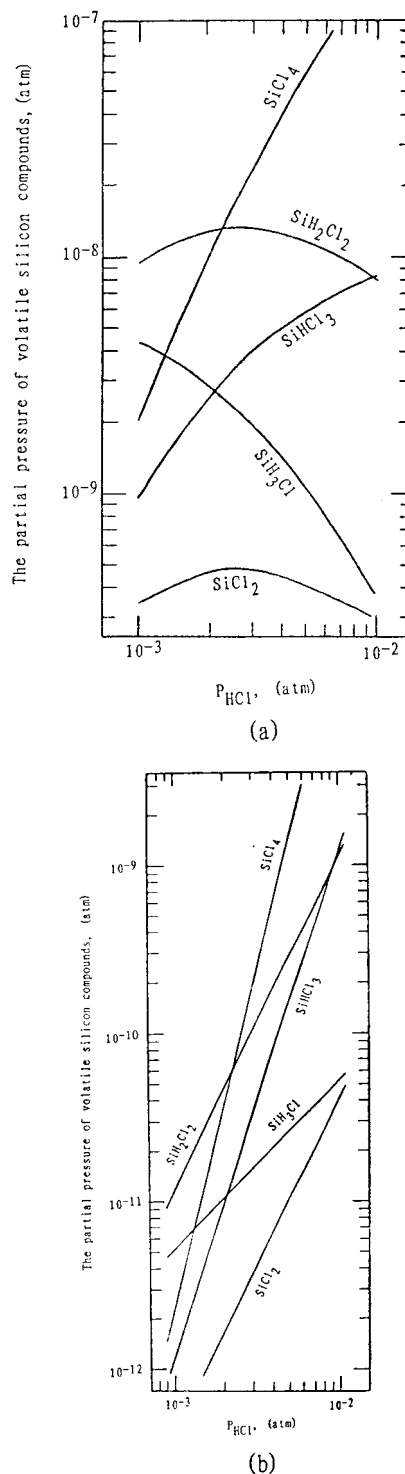

(a)

(b)

Figure 2. The calculated dependence on P_{HCl} of the silicides formed in the tube wall reactions at $T = 1000$ K and at $P_{H_2} = 1$ atm. in the SiO_2–H_2–HCl system: (a) in a dry system, $P_{H_2O}^0 = 0$ and (b) in a wet system, $P_{H_2O}^0 = 1$ ppm.

then n_{Si}, the mole number of Si atoms deposited in the half growing epilayer per unit time, is

$$n_{Si} = \frac{\rho s \mu_{(HCl)}\overline{\alpha_{Si}}}{2N^0}$$

where N^0 is the Avogadro number. Because $\mu_{(HI)}$ depends on P_{AsCl_3}, we can write, on the basis of DiLorenzo's experimental data[3] at 710 °C for films on (100), the relationship between the

two approximately as follows:

$$\mu_{(HCl)} = 0.066 + 0.066 \times \frac{2}{3}\left(\frac{P_{AsCl_3} - 2.5 \times 10^{-3}}{2.5 \times 10^{-3}}\right) =$$

$$0.066\left[1 + \frac{2}{3}\left(\frac{P_{HCl} - 2.5 \times 10^{-3}}{2.5 \times 10^{-3}}\right)\right] \quad \text{(the unit is } \mu m/min)$$

These Si atoms deposited are derived from the molecules of volatile silicides in the gas stream flowing over the surface of the substrate per unit time (equivalent to the flow V). This portion of Si, if it is converted into the volatile silicides in the original stream, has its partial pressure $P_{Si(d)}$

$$P_{Si(d)} = \frac{n_{Si}RT_r}{V\frac{T_r}{T}} = n_{Si}\frac{RT}{V} =$$

$$\frac{\rho s\overline{\alpha_{Si}}RT}{2\,N^0 V}\left[0.066\left(1 + \frac{2}{3} \times \frac{P_{HCl} - 2.5 \times 10^{-3}}{2.5 \times 10^{-3}}\right)\right] \quad (1.2)$$

where T_r is the growth temperature, V is the flow measured at room temperature T, and $V(T_r/T)$ expresses the change in the flow caused by the rise of temperature in the reaction tube. The $\mu_{(HCl)}$, T, V, S, and T_r variables are conditioning each other. Because Ashen's paper[2] does not contain the complete set of these data, we have to use DiLorenzo's typical data;[3] thus, $S \approx 4\ cm^2$, $V = 300\ cm^3/min$, and $T_r = 710\ °C$. Then, from silicon conservation at the "halfway line" we have

$$\sum P_{Si(V)} = P_{SiCl_4} + P_{SiHCl_3} + P_{SiH_2Cl_2} + P_{SiH_3Cl} +$$

$$P_{SiCl_2} + P_{Si(d)} = \left\{K_{1.1}P_{HCl}^4 + K_{1.2}P_{HCl}^3 + \right.$$

$$K_{1.3}P_{HCl}^2 + K_{1.4}P_{HCl} + K_{1.5}P_{HCl}^2 +$$

$$\left.\frac{\rho SRT}{2N^0 V}\left[0.066\left(1 + \frac{2}{3}\frac{P_{HCl} - 2.5 \times 10^{-3}}{2.5 \times 10^{-3}}\right)\right]\right\}\overline{\alpha_{Si}} = \lambda_{(HCl)}\overline{\alpha_{Si}}$$

$$(1.3)$$

where $\lambda_{(HCl)}$ expresses the ratio between $\overline{\alpha_{Si}}$ and $\sum P_{Si(v)}$, and is a function of HCl. Because Ashen et al. gave no indication as to the quantity of silicon they put into the gallium source,[2] we set $K^\# = 8 \times 10^{-6}$; substituting it into (1.1) and (1.3), and then reducing the result, we obtain

$$\overline{\alpha_{Si}} = \frac{2 \times 8 \times 10^{-6} \times P_{HCl}}{\lambda_{(HCl)}} \quad (1.4)$$

Thus, $\overline{\alpha_{Si}}$ as a function of P_{HCl} follows. Figure 3 gives a comparison between this calculated curve and Ashen et al.'s experimental result.

Although the quantities of all the silicides as well as α_{Si} change with P_{HCl} (see Figure 2), the $\overline{\alpha_{Si}}$ we calculated for different P_{HCl} are always in equilibrium with the corresponding quantity of every silicide. The silicides themselves are also in equilibrium with one another (see the proof of the compatibility relationship[1]). The calculated result expresses harmonic, common contributions from them, reflecting the actual case. However, for the algorithm of dominant species, the α_{Si} can only be in equilibrium with one species. In addition, this algorithm can be generalized to calculate $\lambda_{(T)}$ (the argument is temperature).

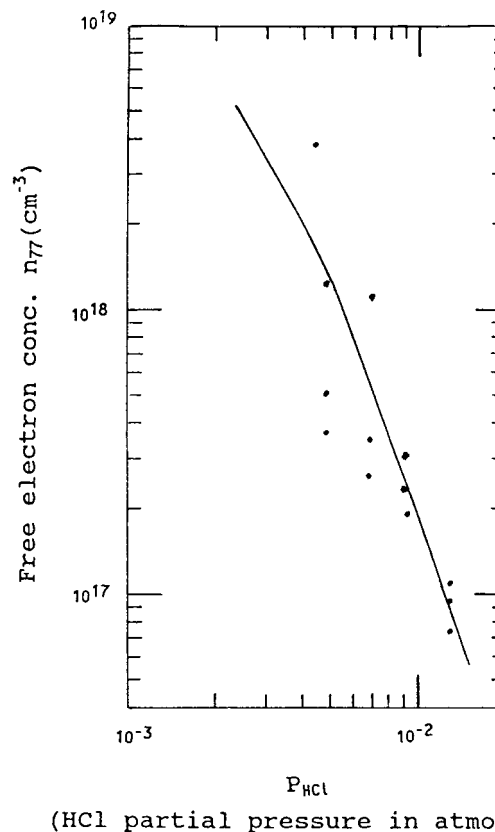**Figure 3.** A comparison between this calculated result (solid line) and Ashens et al.'s experimental data[2] (points).

Here, we can derive two conclusions. The first is in regard to calculation error. From the silicon conservation in (1.3), we can clearly see that, at a fixed P_{HCl}, the more silicide species we calculate, the smaller the α_{Si}, because under that condition their total amount $\sum P_{Si(v)}$ is constant. If a certain major species is neglected, or if the total volatile silicon is taken for the quantity of one species (as in the algorithm of dominant species), as a matter of course a larger positive error (the calculated value is greater than the true value) will be produced. As there are always some neglected species in any calculation, we can draw a conclusion: the calculation always gives a positive error.

The second involves the inhibition mechanism. Through calculation we find that the Si incorporated into the epilayer occupies about 40% of $\sum P_{Si(v)}$ when $P_{HCl} = 2.5 \times 10^{-3}$, about 8% when $P_{HCl} = 5 \times 10^{-3}$, about 1% when $P_{HCl} = 1 \times 10^{-2}$, and only about 0.3% when $P_{HCl} = 1.5 \times 10^{-2}$. These data show the inhibitory action of HCl on the Si contamination discussed here. However, the Si contamination from the quartz reactor is inhibited by oxygen.[1] The inhibition mechanisms of the two are different; the support Ashen et al.'s experiment[2] gives to the Si contamination model then turns out to be rather weak. This also shows that the higher P_{HCl} in VPE process, the more uniform α_{Si} in the film.

Example 2. Calculation of the Mole Fraction Effect in the GaAs VPE Process. Now we consider DiLorenzo's well-known experiment.[3]

Seeing the shortcoming of the dominant-species algorithm, researchers presented a algorithm considering four species ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2, and SiH_3Cl) for calculating the effect in 1971:[4,7]

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

At that time, the compatibility relationship had not been presented yet. The lack of the guidline resulted in defects in their derivation of the above formula. In ref 1, we have reduced it into

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

In this way, so long as we find P_{H_2O}, (the equilibrium quantity of water), the α_{Si} can be calculated. The things not only become much simpler, but also become more direct. To wit, previously we must solve a third-power equation first to find P_{H_2O},[4,7] but in this algorithm, the solution of α_{Si} is achieved with one step.

First, let us calculate P_{H_2O}.

The total amount of water formed in the tube wall reactions, namely, $P_{H_2O(g)}$, is just twice the total amount of the concurrently formed species, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, and $SiCl_2$.[4,7] These silicides are, respectively, in equilibrium with the tube wall, but in light of the compatibility relationship, they are also, respectively, in equilibrium with the silicon atoms in the epilayer. Hence, their quantities can be respectively expressed in α_{Si}; in this way, the number of unknowns can be reduced. Furthermore, their total amount can be expressed by using the same formula as that (1.3) in Example 1. But, in Example 1, the $\Sigma P_{Si(v)}$ is a given quantity, in contrast, the $\Sigma P_{Si(v)}$ in this example is an unknown to be calculated. Those Si-containing species formed in tube wall reactions are the species that contribute to $\Sigma P_{Si(v)}$. The more species that are formed, the more the $\Sigma P_{Si(v)}$, and the greater the amount of water and the smaller the α_{Si}. An unexpected result is that the greater the number of the silicide species that are formed in tube wall reactions, the smaller the quantity of Si contamination. The calculation also gives a positive error. The total amount of the formed water is

$$P_{H_2O(g)} = 2\lambda_{(HCl)}\overline{\alpha_{Si}} \tag{2.1}$$

Ga_2O is not considered, because during epitaxy the surface of the Ga source is covered with GaAs. The oxygen contained in the hydrogen is entirely converted into water under epitaxial conditions. We suppose that the initial total amount of water, $P_{H_2O}^0$, provided by the oxygen and water both contained in the input hydrogen is 0.3 ppm. This value is not given in ref 3, and is estimated to be lower here, because DiLorenzo used two Pd diffusers and his gas-handling system was enclosed in a box purged with filtered nitrogen.

There is another source of oxygen. We know that PCl_3 is easily oxidized. There is already a report on the existence of oxygen in PCl_3.[8] $AsCl_3$ is a compound similar to PCl_3. Therefore, we surmise that, in $AsCl_3$, there is some unknown species containing oxygen. The species has almost the same vapor pressure as $AsCl_3$, hence, it cannot be removed by distillation. We further surmise that the species is dissolved in $AsCl_3$ with saturated concentration. Then it, along with $AsCl_3$ at the fixed proportion, enters the reaction tube, and at the source temperature, the oxygen in it is converted into H_2O. If the thermodynamic data we now use are regarded as exact, after detailed calculation we find: only by assuming that each mole of $AsCl_3$ provides 5×10^{-4} mole of oxygen atom can the
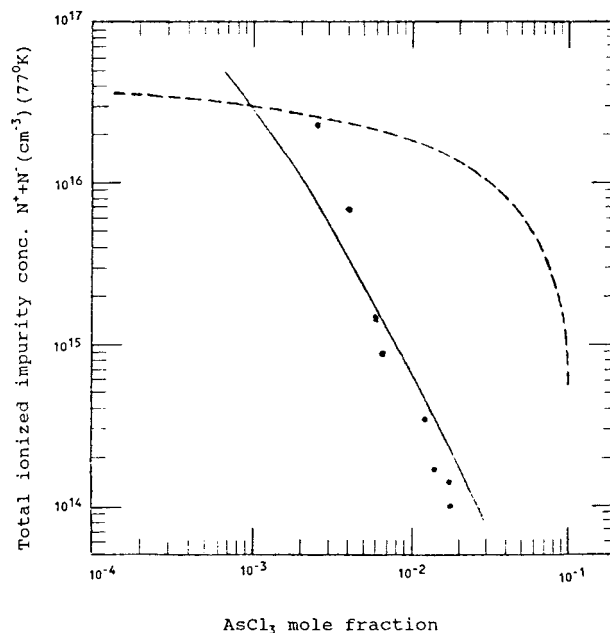

Figure 4. A comparison between two calculations, (dashed line) Rai-Choudhury's[7] and (solid line) this author's, against DiLorenzo's data[3] for the films grown on the (100) (points).

calculated curve be agreeable to the experimental data in a better way. The water quantity provided by the oxygen is then

$$P_{H_2O}^{\#} = 5 \times 10^{-4}P_{AsCl_3} = 5 \times 10^{-4}P_{HCl}$$

The equilibrium quantity of water in the reaction tube is

$$P_{H_2O} = P_{H_2O(g)} + P_{H_2O}^O + P_{H_2O}^{\#} =$$
$$2\lambda_{(HCl)}\overline{\alpha_{Si}} + 0.3 \times 10^{-6} + 5 \times 10^{-4}P_{HCl}$$

Substituting it into (2.3), we have

$$\overline{\alpha_{Si}} = \frac{K_{Si(s \cdot H_2O)}}{[2\lambda_{(HCl)}\overline{\alpha_{Si}} + 0.3 \times 10^{-6} + 5 \times 10^{-4}P_{HCl}]^2} \tag{2.2}$$

Figure 4 gives a comparison between two calculations, Rai-Choudhury's[7] and this author's.

For Rai-Choudhury's curve, the growth temperature is 1000 °K, but the substrate temperature in DiLorenzo's experiment is 983.15 °K; next, he assumed that the initial water amount is $P_{H_2O}^0 = 1$ ppm. However, these two points are of no importance. The key to the distinct improvement of the calculation is assuming that there is some oxygen-containing species dissolved in $AsCl_3$. Conversely, the good calculated result also proves the existence of the species. As it is difficult to analyze oxygen chemically, such a proof turns out to be even more important.

Concluding Remarks

This paper further demonstrates that the compatibility relationship is the basis of all the correct algorithms for the complex system.

References and Notes

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(7) Rai-Choudhury, P. *J. Cryst. Growth* **1971**, *11*, 113.

(8) Hales, M. C.; Knight, J. R. *J. Cryst. Growth* **1979**, *46*, 582.