Hydrogenation Reactions and Their Kinetics for $\text{SiCl}_4(\text{g})\text{--H}_2(\text{g})$ and $\text{SiCl}_4(\text{g})\text{--Si(s)}\text{--H}_2(\text{g})$ Systems Using a Fixed Bed Type Reactor

Masahito Sugiura[†], Hirotaka Kurita^{††}, Takuo Nisida[†] and Akio Fuwa

Department of Materials Science and Engineering, Waseda University, Tokyo 169, Japan

Two kinds of hydrogenation reaction of $\text{SiCl}_4(\text{g})$, i.e.:

and

have been studied under various inlet gas compositions and temperatures in a fixed bed reactor at an atmospheric pressure and without any catalyst addition in order to elucidate their intrinsic reaction kinetics in this investigation. A higher conversion rate has been obtained in the latter gas-solid reaction scheme. A segment compartment model has been used to analyse the reactor performance of a plug flow type for these conversion reactions. A second order, reversible rate equation for the former gas-gas reaction has been assumed and adapted in the rate expression, which has been then used in the reactor performance model calculation. For the latter gas-solid reaction, the two step-wise reaction mechanism; i.e. the first gas-gas reaction step to produce $\text{HCl}(\text{g})$ and the second gas-solid reaction step of this $\text{HCl}(\text{g})$ with Si(s) with a topo-chemical rate model, has been adapted in the rate expression, which was then used in the reactor performance calculation. There have been shown good correspondence between the experimental results and the reactor performance calculation using these postulated reaction rate equations.

(Received March 12, 1992)

Keywords: silicon, hydrogenation, conversion, trichloro-silane, silicon tetra-chloride, kinetics, reaction model

I. Introduction

The Siemens process has been employed for production of the majority of poly-crystalline silicon used in electronic industries. In this process, ultra-high purity silicon is precipitated onto hot silicon-made filaments in a bell jar-type reactor through the chemical vapor deposition reaction of highly purified $\text{SiHCl}_3(\text{g})$, mixed with $\text{H}_2(\text{g})$, at temperatures of 1323 to 1423 K. Plausible over-all reactions for this silicon precipitation process can be described as; $\text{SiHCl}_3(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{Si(s)} + 3\text{HCl}(\text{g})$, and/or $4\text{SiHCl}_3(\text{g}) \rightarrow \text{Si(s)} + 3\text{SiCl}_4(\text{g}) + 2\text{H}_2(\text{g})$, and/or $2\text{SiHCl}_3(\text{g}) \rightarrow \text{Si(s)} + \text{SiCl}_4(\text{g}) + 2\text{HCl}(\text{g})$ ⁽¹⁾. The details of these precipitation reaction schemes are not known at present. However, these reactions do not attain equilibria in the reactor, and the overall Si(s) recovery from $\text{SiHCl}_3(\text{g})$ is said about 27 percent by weight⁽²⁾. Thus, about 13 tons of SiCl_4 is the by-product of the production of 1 ton of ultra-high purity Si. The conversion of this SiCl_4 into SiHCl_3 , which is called hydrogenation reaction, is highly desirable and has been under investigation from an economic standpoint of the Siemens process⁽³⁾: the one route is the hydrogenation reaction of $\text{SiCl}_4(\text{g})$ with $\text{H}_2(\text{g})$, which is called here the gas-gas reaction, i.e. $\text{SiCl}_4(\text{g})$

+ $\text{H}_2(\text{g}) \rightarrow \text{SiHCl}_3(\text{g}) + \text{HCl}(\text{g})$; the other route is to use this $\text{SiCl}_4(\text{g})$ as the reactant source of chlorine, together with $\text{H}_2(\text{g})$, at the chlorination stage of metallic grade silicon, which is called here as the gas-solid reaction, i.e. $\text{Si(s)} + 3\text{SiCl}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow 4\text{SiHCl}_3(\text{g})$. Among the publicized investigations⁽³⁾⁻⁽⁷⁾, Ingle and Peffley made a detailed study on hydrogenation reaction of the second route of the gas-solid reaction in a fluidized bed reactor at various pressures and on the effect of CuCl catalyst addition⁽⁷⁾. From their result, it has been believed that the gas-solid reaction is the two step-wise, sequential reaction as follows: the first step is the reaction of $\text{SiCl}_4(\text{g})$ with $\text{H}_2(\text{g})$ to produce $\text{SiHCl}_3(\text{g})$ and $\text{HCl}(\text{g})$ and the second step is the reaction of Si(s) with the $\text{HCl}(\text{g})$ which has been just produced in the preceding first step, thereby producing $\text{SiHCl}_3(\text{g})$ and $\text{SiCl}_4(\text{g})$. Without CuCl catalyst addition, the first gas-gas reaction step is the slower, rate determining step; whereas with the CuCl catalyst addition, the second step becomes the slower reaction step.

In the present investigation, these two kinds of hydrogenation reactions described, i.e.; $\text{SiCl}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{SiHCl}_3(\text{g}) + \text{HCl}(\text{g})$ and $\text{Si(s)} + 3\text{SiCl}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow 4\text{SiHCl}_3(\text{g})$, have been studied, using a fixed bed reactor, at an atmospheric pressure and without any catalyst addition, so that the intrinsic reaction kinetics of these reactions could be elucidated. On the assumption that the production rate of $\text{SiHCl}_3(\text{g})$ in the gas-gas reaction scheme can be described by a reaction rate equation of second order⁽⁸⁾, the rate constant of the gas-gas reaction has been

[†] Graduate Student, Waseda University.

^{††} Graduate Student, Waseda University. Present address: Yamaha Motor Co., Ltd., Shizuoka 438, Japan.

derived from reactor performance analysis using a segment compartment model of a fixed bed reactor of a plug flow⁽⁹⁾⁽¹⁰⁾. Next, the gas-solid reaction of Si(s) with $\text{SiCl}_4(\text{g})$ and $\text{H}_2(\text{g})$ has been analysed using the reactor performance analysis of the segment compartment model, where the following sequential, two step reaction scheme was assumed: i.e. the first step is to produce $\text{SiHCl}_3(\text{g})$ and HCl(g) , and the second step is the reaction of Si(s) with the HCl(g) which had been derived from the first gas-gas reaction step, thereby producing additional $\text{SiHCl}_3(\text{g})$ and $\text{H}_2(\text{g})$. That is, the HCl(g) concentration in respective compartment was calculated from the result of the kinetic analysis of the first gas-gas reaction study, which was then to react with Si(s) . Topo-chemical reaction kinetic model of a surface reaction control⁽⁸⁾ was used as the rate equation incorporated in the reactor performance model and chlorination reaction of Si(s) of the first order with respect to HCl(g) to produce $\text{SiHCl}_3(\text{g})$ and $\text{H}_2(\text{g})$ were assumed. Through a numerical calculation with a computer for the best-fit with a minimum deviation with experimental results, rate constant of the first order with HCl for the second chlorination reaction step was evaluated.

II. Experimental Procedures

Experimental apparatus: the experimental apparatus used was consisted of reactant gas supplies and their flow controllers, a fixed bed reactor in an electric furnace with a temperature controller, a on-line gas-chromatograph and exhaust gas treatment columns. Figure 1 shows a schematic illustration of the experimental apparatus used in this study. The reactant gases were $\text{H}_2(\text{g})$ of 5 nines

purity and $\text{SiCl}_4(\text{g})$ of 4 nines purity. $\text{H}_2(\text{g})$ was passed through a mass flow controller and mixed with $\text{SiCl}_4(\text{g})$ evolved from its evaporator held at a certain, fixed temperature in order to produce an experimental mixture of $\text{H}_2(\text{g})$ and $\text{SiCl}_4(\text{g})$. The mixed reactant gas was flown into the top of the quartz-made fixed bed reactor of 5.5×10^{-2} m high and 3.1×10^{-2} m in diameter.

In the hydrogenation reaction study of the gas-gas reaction, the mixed reactant gas was passed through the fixed bed reactor of 55 mm high packed with silica balls of 5×10^{-3} m in diameter and the void fraction, $\epsilon=0.481$.

In the gas-solid reaction scheme, the reactant gas mixture was passed through sized, solid silicon particles of a fixed height of 5.5×10^{-2} m in the reactor. The void fraction, ϵ , measured here was 0.523. Solid silicon particles were prepared, crushed from ultra-pure, poly-crystalline silicon chunks of 11 nines and sized from 3.5 to 8.0 mesh. The surface treatment for removal of silicon oxide layers by solutions of hydrofluoric, nitric and acetic acids was provided before hydrogenation experiments. These silicon particles were then mixed with silica balls of 5×10^{-3} m in diameter in the same amount as the silicon, so as to attain a smooth gas flow in the fixed bed reactor.

For preservation of product gas compositions at experimental temperatures, the product gas from the reactor was quenched at a water-cooled flow outlet located just beneath the reactor in the furnace. The product gas was then flown through stainless-steel piping path and introduced into the on-line gas-chromatograph for gas compositional analysis. The outlet gas piping path was heated at about 340 K by silicon rubber heating windings for prevention of condensation of the product gases. Then, the gas was treated by a cold trap columns held at

Fig. 1 A schematic illustration of the experimental apparatus.

223 K, made of dry ice and ethanol, tetra-hydro-flane absorbent and NaOH solution before exhausted into the atmosphere. The column used in the gas chromatograph was made of stainless-steel tubing, 3×10^{-3} m ID and 4.0 m long, filled with 15 weight percent of Silicone DC-QF1. The carrier gas was He of 6 nines purity and a thermal conductivity detector was used. An area integrator was used for a quantitative gas composition measurement. Standard gases, SiHCl_3 and HCl , of 6 nines, supplied from Tri-Chemical Co. (Kanagawa Pref. Japan) were used to derive their standard retention time and area for quantitative measurement by the gas chromatograph.

Experimental condition: The experimental hydrogenation reaction temperatures in the first gas-gas reaction was 1023, 1073, 1103 and 1123 K and that of the second gas-solid reaction 1073 K. The ratio of $\text{SiCl}_4(\text{g})$ to $\text{H}_2(\text{g})$ in the inlet gas mixture was set at 16.62 to 83.38, 34.59 to 65.41 or 47.18 to 52.82. The total experimental pressure in the reactor was one atmosphere. The apparent residence time was varied from about 2 to 14 seconds by changing inlet flow rate of an experimental gas mixture.

III. Experimental Result and Reaction Analysis

1. The gas-gas reaction

In this reaction scheme, hydrogenation reaction between $\text{SiCl}_4(\text{g})$ and $\text{H}_2(\text{g})$ was studied and the product gases, i.e. $\text{SiHCl}_3(\text{g})$ and $\text{HCl}(\text{g})$, from the reactor were analysed by the on-line gas chromatograph. Figure 2(1), (2) and (3) show typical experimental results

of the outlet, mole fractions of these respective gases as function of residence time at different inlet gas mixture and 1073 K. Nearly equal amounts of both $\text{SiHCl}_3(\text{g})$ and $\text{HCl}(\text{g})$ were produced in this gas-gas reaction scheme, irrespective of inlet gas mixture ratio. From these observation, the gas-gas reaction proceeds in the following chemical stoichiometry under the experimental condition of this study:

Figure 3 shows the conversion rate of $\text{SiCl}_4(\text{g})$ into $\text{SiHCl}_3(\text{g})$, which is defined as the ratio of SiHCl_3 moles at the outlet over SiCl_4 moles at the inlet. Figures 4 and 5 shows experimental results of outlet gas mole fractions and the conversion at various temperatures, respectively, where the inlet reactant gas ratio was fixed at inlet $\text{SiCl}_4/\text{H}_2 = 0.3459/0.6541$.

After due consideration of several plausible rate equations to be employed in the kinetic analysis, a second order, reversible rate equation has been assumed and adapted in this study. Thus, rates of forward and backward gaseous reactions are expressed by r_I and r_{II} , respectively, as follows:

$$r_I = (P_T/RT)^2 k_I N_{\text{SiCl}_4} N_{\text{H}_2} = k_I C_{\text{SiCl}_4} C_{\text{H}_2} \quad (2)$$

$$r_{II} = (P_T/RT)^2 k_{II} N_{\text{SiHCl}_3} N_{\text{HCl}} = k_{II} C_{\text{SiHCl}_3} C_{\text{HCl}} \quad (3)$$

These rates are expressed in dimension of moles/ L_{GAS}^3/t , from which the evolution rates of respective gaseous species must be derived for the analysis of kinetics using the segment compartment model of this study. The seg-

(1)

Fig. 2 Mole fractions of respective product species under various input ratios of SiCl_4 to H_2 in the gas-gas reaction as a function of residence time at 1073 K. (1) at inlet $\text{SiCl}_4/\text{H}_2=0.3459/0.6541$, (2) at inlet $\text{SiCl}_4/\text{H}_2=0.4718/0.5282$, (3) at inlet $\text{SiCl}_4/\text{H}_2=0.1662/0.8338$

Fig. 3 SiCl₄ conversion in the gas-gas reaction as a function of residence time at 1073 K. Fig. 4. Mole fractions of respective product species at different temperatures in the gas-gas reaction as a function of residence time at inlet SiCl₄/H₂=0.3459/0.6541.

Fig. 5 SiCl_4 conversion as function of residence time in the gas-gas reaction at inlet $\text{SiCl}_4/\text{H}_2=0.3459/0.6541$.

ment compartment model⁽¹⁰⁾ is described in the Appendix and used in this study for evaluation of reactor performance and derivation of rate constants, k_I and k_{II} . The evolution rates of forward and backward reactions in void portion of a reactor are related to r_i and given by:

$$R_i = \varepsilon \cdot r_i \quad (4)$$

i.e.

$$R_I = \varepsilon (P_T/RT)^2 k_I N_{\text{SiCl}_4} N_{\text{H}_2} = \varepsilon k_I C_{\text{SiCl}_4} C_{\text{H}_2} \quad (5)$$

$$R_{II} = \varepsilon (P_T/RT)^2 k_{II} N_{\text{SiHCl}_3} N_{\text{HCl}} = \varepsilon k_{II} C_{\text{SiHCl}_3} C_{\text{HCl}} \quad (6)$$

Then, these evolution rates of respective gaseous species can be expressed as follows:

$$R_{\text{HCl}} = R_I - R_{II} \quad (7)$$

$$R_{\text{H}_2} = -R_I + R_{II} \quad (8)$$

$$R_{\text{SiHCl}_3} = R_I - R_{II} \quad (9)$$

$$R_{\text{SiCl}_4} = -R_I + R_{II} \quad (10)$$

For the reactor performance analysis here, eqs. (11) and (12) are used here, which are given by (A8) and (A9), respectively:

$$G_{j+1} - G_j = (\sum R_{j,i})(A_R \Delta z_j) \quad (11)$$

$$N_{j+1,i} - N_{j,i} = [(A_R \Delta z_j)/G_j][R_{j,i} - N_{j,i}(\sum R_{j,i})] \\ = [(A_R \Delta z_j)/G_j](R_{j,i}) \quad (12)$$

In the computation in this study, Δz_j was set constant, 5.5×10^{-4} m, thereby dividing the fixed bed into 100 segment compartments. The boundary condition at the inlet, G_0 and $N_{0,i}$, were known initial total flow rate and

input gas compositions, respectively. $N_{\text{exit},i}^{\text{cal}}$, where i is $\text{SiCl}_4(\text{g})$, $\text{SiHCl}_3(\text{g})$ or $\text{HCl}(\text{g})$, is the mole fraction of respective gaseous species at the reactor exit, that has been calculated as function of the rate constants, k_I and k_{II} . The ratio of k_I/k_{II} was taken to be $1/K_{\text{eq}}$, where K_{eq} is the equilibrium constant of the gas-gas reaction at an experimental temperature. K_{eq} value was obtained using the JANAF thermochemical data⁽¹¹⁾. Local values for G_j and $N_{j,i}$ were calculated by the above mentioned eqs. (11) and (12) incorporating postulated rate equations with rate constants, k_I and k_{II} . Computation with different k_I value was conducted on a trial-and-error base, until the deviation of $N_{\text{exit},i}^{\text{cal}}$ from $N_{\text{exit},i}^{\text{exp}}$, those obtained experimentally, could be minimized. The best-fit k_I value is the one which brings about the minimum difference between $N_{\text{exit},i}^{\text{cal}}$ and $N_{\text{exit},i}^{\text{exp}}$. Figure 6 shows an Arrhenius plot of the best-fit rate constants at these experimental temperatures. k_I and k_{II} can be expressed as function of temperature as follows:

$$k_I = k_I^0 \exp(-E/RT) \\ = 1.04 \times 10^{17} \exp(-2.80 \times 10^8/RT) \quad (13)$$

$$k_{II} = k_{II}^0 \exp(-E/RT) \\ = 5.00 \times 10^{15} \exp(-2.19 \times 10^8/RT) \quad (14)$$

The calculated conversion rate of $\text{SiCl}_4(\text{g})$ and gas compositions are shown by solid lines in Figs. 2 to 5 under these experimental hydrogenation conditions specified in these figures. As seen from these figures, there are seen good correspondence between the experimental results and the calculated results.

Fig. 6 An Arrhenius plot of k_I and k_{II} for the gas-gas reaction.

2. The gas-solid reaction

In this reaction scheme, sized silicon particles, mixed with silica balls, were placed in a fixed bed reactor and reacted with the gas mixture of $\text{SiCl}_4(\text{g})$ and $\text{H}_2(\text{g})$. The inlet gas mixture ratio of $\text{SiCl}_4(\text{g})$ to $\text{H}_2(\text{g})$ was the same as in the gas-gas reaction scheme. Figure 7(1), (2) and (3) show the experimental results under the various conditions. Figure 8 shows the conversion rate of $\text{SiCl}_4(\text{g})$ into $\text{SiHCl}_3(\text{g})$. Compared with the conversion obtained in the previous gas-gas reaction, a higher conversion rate of

$\text{SiCl}_4(\text{g})$ into $\text{SiHCl}_3(\text{g})$ was observed in this gas-solid reaction scheme. Higher conversion was obtained at a larger ratio of $\text{SiCl}_4(\text{g})/\text{H}_2(\text{g})$ in the inlet gas mixture. As mentioned before, the authors considered that this gas-solid reaction proceeds in the two steps in series: the first step is considered here as the slower reversible gas-gas reaction, where $\text{SiCl}_4(\text{g})$ reacts with $\text{H}_2(\text{g})$ to produce $\text{SiHCl}_3(\text{g})$ and $\text{HCl}(\text{g})$ as

Then, in the second step, $\text{HCl}(\text{g})$, which is the product in the first gas-gas reaction, reacts with $\text{Si}(\text{s})$ to produce $\text{SiHCl}_3(\text{g})$. There has been no sufficient information available in the literature with respect to rate expression or kinetics on the chlorination reaction of $\text{Si}(\text{s})$ with $\text{HCl}(\text{g})$ for production of $\text{SiHCl}_3(\text{g})$. In this study, the following chlorination reaction for $\text{SiHCl}_3(\text{g})$ and $\text{H}_2(\text{g})$ evolution are assumed, so that further analysis could be proceeded;

Furthermore, the reaction rate of the first order with respect to $\text{HCl}(\text{g})$ on the silicon particle surface⁽⁸⁾ is assumed here for silicon chlorination reaction (15), which will be given by the following rate equation expression:

$$R_{III} = R_{Si} = [\phi(1 - \epsilon)/x_0] k_{III} C_{HCl} \quad (16)$$

where

(1)

Fig. 7 Mole fractions of respective product species under various input ratios of SiCl_4 to H_2 in the solid-gas reaction as function of residence time at 1073 K. (1) at inlet $\text{SiCl}_4/\text{H}_2=0.3459/0.6541$, (2) at inlet $\text{SiCl}_4/\text{H}_2=0.4718/0.5282$, (3) at inlet $\text{SiCl}_4/\text{H}_2=0.1662/0.8338$

Fig. 8 SiCl₄ conversion in the gas-gas reaction as a function of residence time at 1073 K.

k_{III} = the rate constants for reaction (15), (m/s)

Then, evolution rate of respective gaseous species can be described by the following equations from reaction stoichiometries:

$$R_{\text{HCl}} = R_{\text{I}} - R_{\text{II}} - 3R_{\text{III}} \quad (17)$$

$$R_{\text{H}_2} = -R_{\text{I}} + R_{\text{II}} + R_{\text{III}} \quad (18)$$

$$R_{\text{SiHCl}_3} = R_{\text{I}} - R_{\text{II}} + R_{\text{III}} \quad (19)$$

$$R_{\text{SiCl}_4} = -R_{\text{I}} + R_{\text{II}} \quad (20)$$

The k_{I} and k_{II} values obtained in the previous section for the gas-gas reaction were used in this gas-solid reaction analysis. The reactor performance computation was done by assigning various value for k_{III} in equations (A8) and (A9), with known inlet composition and flow rate at respective experimental temperature. Local values for G_j and $N_{j,i}$ were calculated by the above-mentioned equations until the outlet of the fixed bed reactor. The best-fit k_{III} value was sought by a trial and error method, which minimized the deviation of $N_{\text{exit},i}^{\text{cal}}$ values from $N_{\text{exit},i}^{\text{exp}}$ in respective temperatures. The best-fit value of k_{III} is 4.0×10^{-4} m/s.

Using this best-fit k_{III} value, the calculated composition and SiCl₄ conversion rate are also shown in Figs. 7(1) to (3) and Fig. 8, respectively. As seen from these figures, there is a fairly good correspondence between the experimental result and the calculated one, although the agreement is rather poor in general when compared with the gas-gas reaction result. The authors consider that the

first reason for this poor agreement is that the compartment reactor model used in analysis of the experimental data assumes the plug flow in one dimensional direction, which may not be appropriate assumption to represent the real complex gas flow in the reactor. The second reason is that the assumption made in rate equation for the gas-solid reaction, i.e. the first order reaction rate to produce SiHCl₃(g) may not be appropriate. The detailed kinetic study of chlorination reaction of solid silicon with hydrochloric gas for production of SiHCl₃(g) and SiCl₄(g) is not available at present, that has made this simple assumption in this investigation. The main reason for this poor agreement is probably due to the second assumption of reaction kinetic model. Further study is needed for elucidation of this chlorination reaction.

IV. Conclusion

In this investigation, for the conversion (hydrogenation) of SiCl₄(g) into SiHCl₃(g), the gas-gas reaction between SiCl₄(g) and H₂(g) and the gas-solid reaction among Si(s), SiCl₄(g) and H₂(g) in a fixed bed reactor were studied at temperatures from 1023 to 1123 K under an atmospheric pressure. Higher conversion was obtained in the gas-solid reaction at the higher temperatures and by using the larger input ratios of SiCl₄(g) to H₂(g). The segment compartment model for one-dimensional, fixed bed reactor of a plug flow was used to describe the reactor performance and to elucidate the reaction rate

constants in the postulated kinetic equations; for the gas-gas reaction, a second order, reversible rate equation has been adapted to elucidate the reactor performance and derive the rate constant, and for the gas-solid reaction, two step-wise reaction mechanism has been adapted to derive the reactor performance and the rate constant of the second chlorination reaction. There have been shown good correspondence between experimental results and calculated results using the postulated rate equations and the segment compartment reactor model.

Appendix

In order to describe time and position dependence of composition and temperature in a reacting system of a fixed bed reactor of plug flow system, a material balance of gaseous species, i , in the gas stream of a constant pressure system with multiple, non-equimolar homogeneous or heterogeneous gas-solid reaction is considered; for simplicity, the system is taken one dimensional with ideal plug flow of gas. As function of time (t) and position (z) with reference to a fixed coordinate, the material balance for each species, i , in the gas stream, can be described as

$$\begin{aligned} (\text{accumulation rate}) = & [(\text{input rate}) - (\text{output rate})] \\ & + (\text{production by chemical reaction}) \end{aligned}$$

In a quantitative expression, it becomes

$$\begin{aligned} \varepsilon(C_{i,t+\Delta t} - C_{i,t})A_R\Delta z \\ = [(J_{i,z} - J_{i,z+\Delta z})]A_R\Delta t + R_iA_R\Delta t\Delta z \end{aligned} \quad (\text{A1})$$

where

$$\begin{aligned} J_i = N_i(G/A_R) - (P_T/RT)D^{\text{eff}}(\partial N_i/\partial z) \\ = \text{molar flux of species, } i, (\text{moles}/L_{\text{SYS}}^2/t) \end{aligned}$$

In a differential form, eq. (A1) becomes as;

$$\varepsilon(\partial N_i/\partial t) = -(\partial J_i/\partial z) + R_i \quad (\text{A2})$$

With substitution of the above-mentioned relations, eq. (A2) becomes

$$\begin{aligned} (\varepsilon P_T/R) - (N_i/T^2)(\partial T/\partial t) + (1/T)(\partial N_i/\partial t) \\ = -N_i[\partial(G/A_R)/\partial z] + (G/A_R)(\partial N_i/\partial z) \\ - (P_T/R)[\partial(D^{\text{eff}}/T)(\partial N_i/\partial z)/\partial z] + R_i \end{aligned} \quad (\text{A3})$$

After summing up all species and using the relation of $\sum N_i = 1$,

$$\partial(G/A_R)/\partial z = (\varepsilon P_T/RT^2)(\partial T/\partial t) + \sum R_i \quad (\text{A4})$$

This equation shows that the molar flow changes as a function of position within a system due to non-equimolar reactions or due to a non steady state temperature change. On substitution of (A4) into (A3),

$$\begin{aligned} (\varepsilon P_T/R)(\partial N_i/\partial t) \\ = -(G/A_R)(\partial N_i/\partial z) + (P_T/R) \\ \times \{ \partial[D^{\text{eff}}/T](\partial N_i/\partial z) \} + R_i - N_i \sum R_i \end{aligned}$$

This equation is a set of simultaneous partial equations for which gas stream compositions can be derived as functions of time and position. Equations (A4) and (A5) can be simplified in the situation of that (i) the reactions are at steady state so that the time derivatives are eliminated, (ii) the convective flow terms are much larger than the diffusion term so that the diffusion term is eliminated, and (iii) the reactions are at an isothermal temperature so that the temperature dependent terms are eliminated. In such a situation, eqs. (A4) and (A5) become as follows, accordingly;

$$d(G/A_R)/dz = \sum R_i \quad (\text{A6})$$

$$(G/A_R)(dN_i/dz) = R_i - N_i(\sum R_i) \quad (\text{A7})$$

Using the simplest finite difference approximation to these derivatives,

$$G_{j+1} - G_j = (\sum R_{j,i})(A_R\Delta z) \quad (\text{A8})$$

$$N_{j+1,i} - N_{j,i} = [(A_R\Delta z)/G_j][R_{j,i} - N_{j,i}(\sum R_{j,i})] \quad (\text{A9})$$

Where subscript j means the value at the j th stage and subscript $j+1$ means the value at the $j+1$ th stage

Equation (A8) states that molar flow changes as a function of position due to non equimolar chemical reactions. Variable G_j , $N_{j,i}$ and $R_{j,i}$ are all local values (function of position) to be solved numerically by eqs. (A8) and (A9) with the specific boundary conditions.

Nomenclature

- A_R = reactor cross section area, (L_{SYS}^2)
- $C_i = N_i(P_T/RT)$, gas phase concentration, (moles/ L_{SYS}^3)
- D^{eff} = effective diffusivity for gas stream, ($L_{\text{GAS}}^3/L_{\text{SYS}}/t$)
- E = activation energy, (J/mole)
- G/A_R = convective molar flux, (moles/ L_{SYS}^2)
- J_i = molar flux of species, i , (moles/ L_{SYS}^2/t)
- k_I , k_{II} = the forward and backward reaction rate constant, respectively, ($L_{\text{GAS}}^3/\text{moles}/t$, or m/moles/s)
- k_{III} = the rate constants for reaction (15), (m/s)
- L_{GAS} = length dimension in gas phase, (m)
- L_{SYS} = reactor length dimension, (m)
- N_i = mole fraction of species, i (-)
- P_T = total pressure in reactor, (Pa)
- r_i = production rate of species, i (mol/ L_{GAS}^3/t)
- R_i = rate of production of species, i , by chemical reaction, (mol/ L_{SYS}^3/t)
- R = gas constant, (8.3145 J/mol/K)
- t = time, (s)
- T = temperature, (K)
- x_0 = average silicon particle radius, (m)
- z = reactor height, (m)
- Δt = time segment, (s)
- Δz = height segment, (L_{SYS})
- ε = gas void fraction in a reactor, ($L_{\text{GAS}}^3/L_{\text{SYS}}^3$)
- ϕ = shape factor of silicon particles, (-)

REFERENCES

- (1) Japan Electronic Industry Development Association, Research

- Report No. 58-M-212 (1986).
- (2) Y. Abe: Bulletin Japan Inst. Metals, **23** (1984), 765.
- (3) Union Carbide Corp. Final Report, D.O.E./J.P.L. Contract no. 954, 334 (1979).
- (4) J. P. Mui and D. Seyferth: Massachusetts Institute of Technology Final Report, D.O.E./J.P.L. Contract no. 955, 382 (1981).
- (5) J. P. Mui: Solarelectronics, Inc. Final Report, D.O.E./J.P.L. Contract no. 956, 061 (1981).
- (6) J. McCormick, F. Plahutnik, A. Arvidson, D. Sawyer and K. Sharp: Hemlock Semiconductor Corp. Final Report, D.O.E./J.P.L. Contract no. 955, 533 (1982).
- (7) W. M. Ingle and M. S. Peffley: J. Electrochem. Soc., **132** (1985), 1236.
- (8) O. Levenspiel: *Chemical Reaction Engineering*, 2nd Ed., ed. by John Wiley and Sons, New York, (1976).
- (9) H. Kurita: Master of Engineering Thesis, Waseda University, Tokyo, (1991).
- (10) R. H. Spitzer: *Computer Usage in Materials Education*, ed. by G. L. Liedl and K. S. Sree Harsha, Ed. 45, The Met. Soc. Inc. Penn., (1985).
- (11) JANAF Thermochemical Tables, 3rd Ed. J. Phy. Ref. Data, **14**, Supplement no. 1, (1985).